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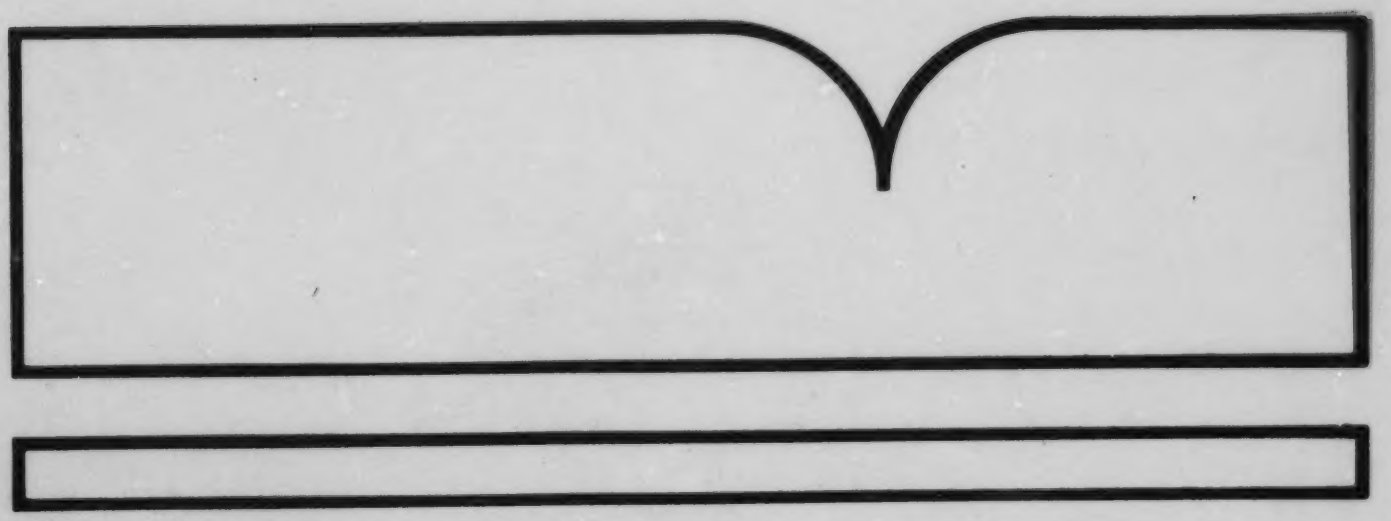

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CHEMICAL RECLAMATION OF SCRAP RUBBER

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A conceptual, commercial-scale plant design was formulated for processing 22,500 t/yr of scrap rubber tires to hydrocarbon fuel gases, oils, petrochemicals (principally ethylene and aromatic liquids), and carbon black. The process is based upon molten salt (zinc chloride) pyrolysis of the rubber, and pyrolysis data obtained in a bench-scale flow apparatus. An economic assessment of the plant was made in terms of late 1979 dollars, for ranges in scrap tire costs and prices for the principal products: carbon black and the fuel gases and oil. Profitability at these 1979 costs and prices is somewhat modest by chemical processing industry standards for new processes, but any increases in energy and carbon black prices would cause favorable changes in this assessment.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study involved the formulation of a conceptualized commercial-scale plant design to process scrap rubber tires for their by-products. The process is based on molten salt pyrolysis of the rubber as well as pyrolysis data from a bench-scale flow apparatus. An economic study was made for scrap tire costs and prices for by-products. The profitability of this process was deemed to be modest but is dependent on increases in energy and carbon black prices. For further information contact the Oil Shale & Energy Mining Branch of the Energy Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research
Laboratory - Cincinnati

ABSTRACT

A conceptual, commercial-scale plant design was formulated for processing 22,500 t/yr of scrap rubber tires to hydrocarbon fuel gases, oils, petrochemicals (principally ethylene and aromatic liquids), and carbon black. The process is based upon molten salt (zinc chloride) pyrolysis of the rubber, and pyrolysis data obtained in a bench-scale flow apparatus. An economic assessment of the plant was made in terms of late 1979 dollars, for ranges in scrap tire costs and prices for the principal products: carbon black and the fuel gases and oil. Profitability at these 1979 costs and prices is somewhat modest by chemical processing industry standards for new processes, but any increases in energy and carbon black prices would cause favorable changes in this assessment.

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1.0 SUMMARY AND RECOMMENDATIONS

A conceptual, commercial-scale plant for converting scrap rubber tires into hydrocarbon gases, oil and carbon black was formulated and evaluated with respect to its economic potential in terms of late 1979 dollars. The conceptual plant processes 2,500 t/yr of scrap tires (68.5 t/d) to 115 MMscf/yr of gas, 1.91 MM gal/yr of oil, and 19.9 MM lb/yr of carbon black. The process is of the semi-batch type, with the tires chopped prior to their conversion in the reactor by molten zinc chloride pyrolysis. The economic analysis was based upon "over the fence" sale of oil and gas for recovery of chemical values (both olefin gases, principally ethylene, and also aromatic liquids). The remaining gas and oil was assigned fuel values. Carbon black is the principal product in terms of both quantity and economic value at current prices.

The commercial plant design was developed primarily on a data base which was generated from a bench-scale experimental set up of the flow type, in a system constructed of 316 stainless steel. Among the data provided by these experiments were the product yields, reactor operating conditions (temperature and molten salt-rubber contact times), salt make-up requirements, and salt reuse data. Suitable reaction temperatures are in the range of 680-752°F (360-400°C).

The primary advantages of this process include:

(a) pyrolysis at moderately low temperatures, due to the catalytic heat transfer action of the molten zinc chloride salt. The carbon black produced in this relatively low temperature range may have special properties.

(b) the ability to convert the scrap rubber to products of commercial value, without grinding the rubber. This fact not only saves in terms of grinding costs, but also reduces the problem of separating the fiberglass tire cord and steel wire from the carbon black.

A principal disadvantage of this type of process is the corrosiveness of the molten salt, but experience at the bench scale on this project indicates this problem can be overcome.

The economic analysis was based on a total investment of $6.93 MM (including 20 percent working capital), straightline depreciation over an 8-year period, 10 percent interest on total investment, construction over a one-year period, and marketability of all products at late 1979 prices (except for the steel wire and fiberglass, both of which were assigned no value). The profitability of the process depends strongly on the values of

the carbon black and of the fuel gases and oil, as well as upon the cost of the scrap, feed tires, and less strongly on the cost of separating (purification) the chemicals from the gas and oil products. The most uncertain parameters in the cost study are the value of the carbon black, the cost of the scrap tires, and the cost of chemical purification. The percent return on investment (ROI) is shown in Table 1.1 for a selected range in each of these parameters. A plant of this size (22,500 t/yr of tires) is profitable for scrap tire costs in the range of 20 $/t or less and with fuel and carbon black values in the range of 3-5 $/MM Btu and 15-21 ¢/lb, respectively, although the profit margin is probably insufficient to attract venture capital under these economic conditions. Fuel and carbon black prices will need to rise considerably for a plant of this size to be profitable if the cost of purchasing and collecting scrap tires should be as high as 40 $/t.

If prices increase in petrochemicals and energy above 1979 levels, one can expect improvements in the profitability numbers given in Table 1.1 for this process. There may then be sufficient incentive to demonstrate this process at a larger scale of operations. It is recommended that provisions for the following tests be included in such a demonstration program:

- the generation of sufficient quantity of carbon black for test marketing in products such as rubber, plastics, ink, and activated carbon. The marketability of the carbon black is the greatest uncertainty in this process, and profitability of the plant is strongly tied to the carbon black product and its price.

- establishment of the fraction of the carbon black which can be recovered in relatively pure form.

- establishment of the effectiveness of the molten salt in the long term, confirmation of the salt make-up requirements, and establishment of the fraction of the salt which must be recovered from the reaction residue for recycle to the reactor.

- establishment of the efficacy of existing screening technology for separating and dealing with the fiberglass fluff.

- acquisition of long-term corrosion testing and system maintenance data.

In view of the somewhat marginal profitability picture for this process at this time (but favorable trends in the prices of its major products), it is further recommended that the economic potential of this process be reassessed in the near future.

TABLE 1.1. RETURN ON INVESTMENT (ROI) FOR SELECTED RANGES IN THE COST AND PRODUCT VALUE PARAMETERS. PLANT CAPACITY = 22,500 T/YR OF TIRES

Case	Tire Cost $/t	Purification Cost* %	Fuel/Value $/MM Btu	Carbon Black Value, ¢/lb	ROI, %
A	0	30.	5.0	21.	15.2%
B	0	90.	5.0	21.	9.9
C	0	30.	5.0	15.	6.9
D	0	30.	3.0	21.	10.7
E	20.	30.	5.0	21.	11.7
F	20.	90.	5.0	21.	6.4
G	20.	30.	5.0	15.	3.4
H	20.	30.	3..0	21.	7.2

*As a percent of the Chemicals Value.

2.0 INTRODUCTION

Interest in the utilization of scrap tires as a source of chemicals, fuel, and carbon black has been increasing in recent years, due not ony to environmental regulations but also to the fact that chemicals and fuels based on petroleum and natural gas have risen in price at rates much greater than the general inflationary trend during the late '70s. Numerous attempts are therefore being made around the industralized world to recover chemical and fuel values from tires (see Berry, and also Gaines and Wolsky, 1979, for a summary of these developments). Most of the current processes being developed for this purpose rely on pyrolysis of the rubber, by one method or another, requiring the heating of the rubber to temperatures in the range of 500-600°C, or above.

There are a number of problems associated with the task of recovering chemicals from tires due to the chemical and physical nature of the tire itself. Tires may contain fiberglass and steel wire. The rubber is formulated to be abrasive resistant, so grinding is difficult and energy intensive. The quality of the main pyrolysis product, carbon black, seems to deteriorate as the pyrolysis temperature is increased. This project set out to develop a process for recovering chemicals from tires which has the potential of avoiding some of these problems. That is, a process was sought which:

- would not require grinding of the rubber tires in order to avoid associated costs and to minimize the task of separating wire and fiber particles from the carbon black.
- would pyrolyze the rubber at relatively low temperatures.
- would produce chemicals and carbon black of marketable quality.

A process route which seemed to satisfy these process objectives in bench-scale work was pyrolysis in molten halo salts (Larsen and Chang, 1976). Such chemistry had earlier been used to produce hydrocarbons in the gasoline-boiling range from coal by Gorin's group at the Consolidation Coal Co. (now Conoco Coal Research)(Office of Coal Research, 1969; Zielke et al., 1966). This work showed that the large coal molecules were rapidly broken into molecules in the gasoline-boiling range, and also a considerable amount of work had been done in order to deal with one of the major disadvantages of processes of this type--the corrosivenes of the molten salts. Early work also indicated that halo salts would also break rubber into gases, a light oil, and carbon black, at temperatures in the range 350-400°C. This project therefore set out to develop the bench-scale data required for the formulation and economic assessment of a conceptual, commercial plant design. The

results presented in this report are based exclusively on the use of zinc chloride as the heat transfer and catalytic agent.

It is normal practice in the chemical process industries to develop a "conceptual process design" in the early stages of an actual project, in order to identify crucial areas requiring further development, to evaluate various process options which may be available, to assess the overall technical feasibility of the project, and lastly, but most importantly, to establish at the outset whether or not the process has the potential for economic profit. In this context, the objective of the work reported on here has been to obtain that bench-scale experimental data required for the formulation and evaluation of a conceptual process design for the conversion of scrap tires to chemical and fuel products by molten salt pyrolysis, and to use this design as a basis for estimating the potential profitability of the process. Experimental results and the associated economic analysis indicate that such a processing plant converting 22,500 t/yr of tires has the potential for profit at 1979 chemical prices, and energy prices of 3-5 $/MM Btu, assuming the carbon black, the major product, is marketable at prices in the range of at least 15 ¢/lb. Although there are a number of process steps requiring demonstration at the pilot plant scale, the biggest unknown at this point in our process is the marketability of the carbon black. A pilot plant is required to generate sufficient quantities of this material for testing its suitability in products such as rubber, ink, and plastics.

Although molten salt technology is not easy, advantages of this process lie in its relatively low operating temperature, in the range of 360-400°C, and the fact that there is no need to pulverize the tires. However, we do chop the tires for compaction purposes, in order to increase the reactor throughput. Further, the relatively large pieces of fiberglass and wire remaining after the chopping operation appear to be readily separated from the carbon residue downstream of the reactor. A test of this separability at the pilot plant scale is desirable.

3.0 A CONCEPTUAL COMMERCIAL PLANT DESIGN

3.1 PLANT SITING

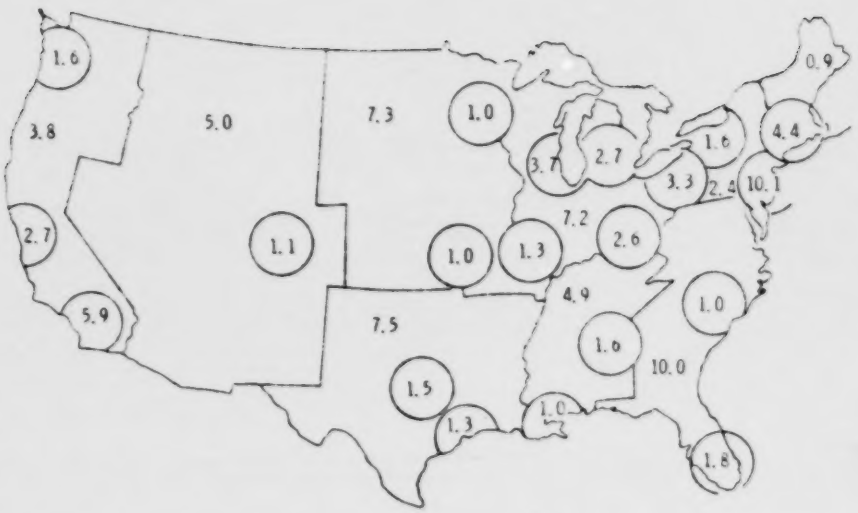
The location of the first plants for recovering fuel and chemical values from rubber tires will be established primarily by availability of feed material, that is, scrap rubber tires, as cost of transport of this material is expected to prohibit long distance shipment of scrap tires. A second factor that may restrict location of tire processing plants is the availability of facilities for separation and purification of chemicals (e.g., ethylene and benzene) from the pyrolysis product gas and oil streams, as the volume of these streams is expected to be too small to warrant the construction of grass roots facilities for this purpose (Larsen, et al., 1977). Markets for the products must also be taken into account. It therefore appears that the most desirable locations for the first generation tire processing plants will be those major population centers which also contain either a petroleum refinery or an ethylene plant, or both. The rate at which tires are discarded by region has been compiled by Pettigrew et al. (1971). These results are shown in Figure 3.1.

Locations of petroleum refineries and ethylene plants are shown in Figures 3.2 and 3.3, respectively, with circles of 150 miles radii. An area of this magnitude is expected to correspond, roughly, to that for which it may be economical to transport scrap tires to processing plants. These areas cover most of the major population centers of the country, although a number, such as the Boston, Atlanta, and Miami areas, are not covered. A location, such as the Gulf Coast (as well as others, see maps, Figures 3.1-3.3), possesses most of the requisites for a tire processing plant: availability of scrap tires, established purification facilities, and markets for the products, gas and oil fuel, petrochemical feed stocks (primarily ethylene and benzene) and carbon black.

3.2 DESIGN BASES

Siting of the facility for "over the fence" disposal of the oil and gaseous products (for purification at an existing facility) in a major population center has therefore guided the selection of the following design bases, assumptions, and constraints:

- Capacity of 68.5 t/d (22,500 t/yr) of scrap tires. At upwards of twenty pounds per tire, and a 75% collection offering, this limits location of the plants to centers of about 2.25MM people or more (DOE, 1979).



The number indicates the percent of the Nation's waste rubber located within the circle. The remaining numbers indicate the percent waste rubber located outside the circles but within the bordered areas.

Figure 3.1. Distribution of Waste Rubber by Region (Pettigrew, 1971)

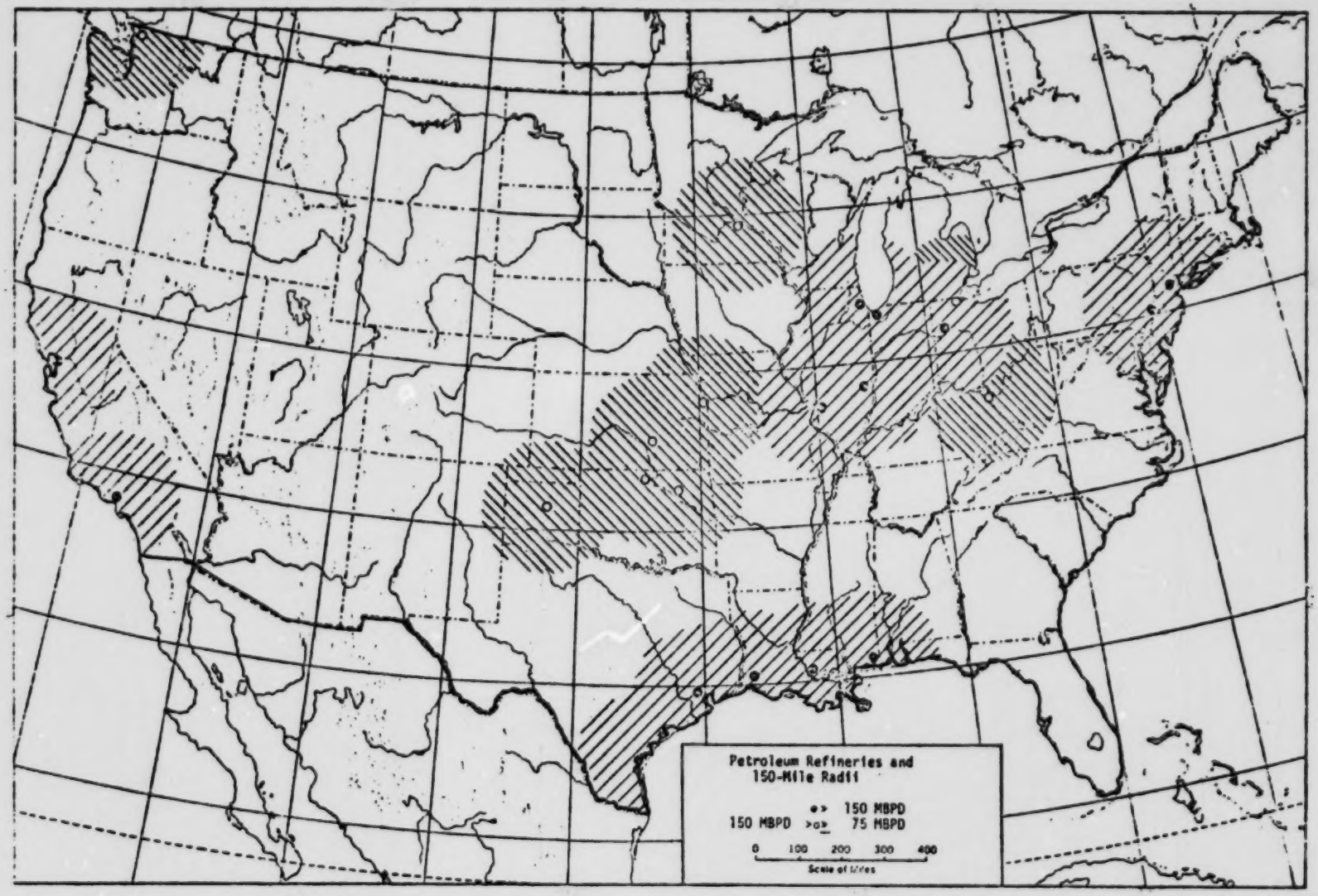


Figure 3.2. Locations of Petroleum Refineries in the Continental United States, with 150 Mile Radii.

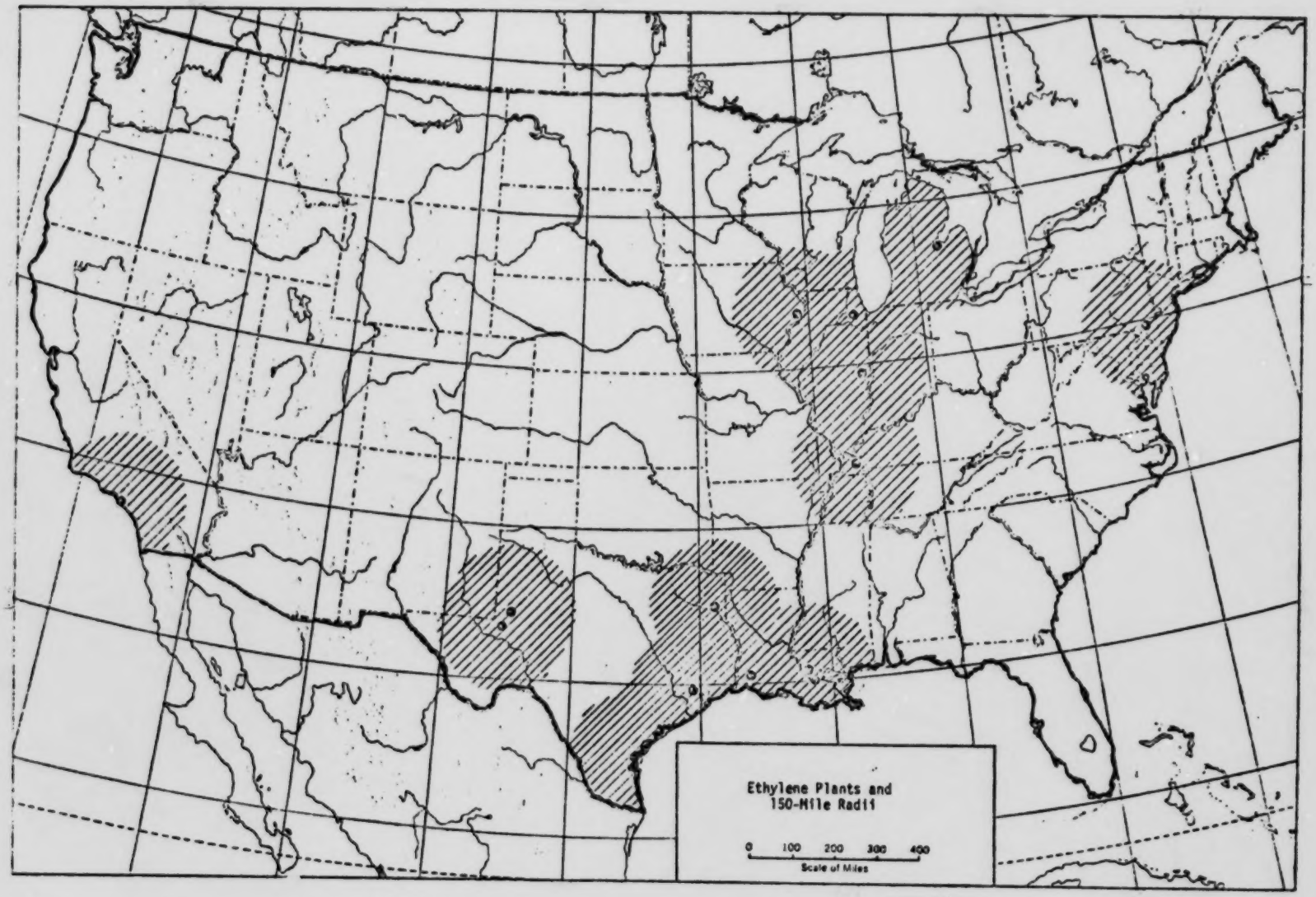


Figure 3.3. Location of Ethylene Plants in the Continental United States, with 150 Mile Radii.

- Single process stream. The scale (68.5 t/d) and available technology do not warrant multiple streams, and it may be that the scale can be doubled or tripled before multiple streams become of interest.

- Batch-type operation for the reactor, but in-line storage tanks and hoppers provide control of the material flow downstream of the reactor so that steady operation and utilization of the processing facilities are achieved.

- 90% on-stream factor, three shifts per day.

- On-site storage facilities or about seven days' production of oil (39,500 gal) and six hours' production of gas (84 mscf). The storage facilities require about 14% of the total fixed capital, and it may be possible to eliminate them altogether through arrangements with the "over the fence" refining and/or ethylene clients.

- Product yields of gas, oil, and carbon black as shown in Tables 3.1-3.3.

- 95% recovery of the carbon black.

- Carbon black can be ground and/or purified to a marketable product.

- Reuse of the zinc chloride catalyst. Limited bench-scale tests (see Section 5.0) indicate that this can be done without appreciable loss of effectiveness for the three cycles of the test. Testing needs to be done on a larger scale and for longer times in order to confirm and extend these results.

Elemental analyses of the product oil and carbon black are shown in Table 3.4. Results of the characterization tests on the crude, unground carbon black are shown in Table 3.5 (McCaffrey, 1979).

3.3 PROCESS DESCRIPTION

The bench-scale experimental work along with related data and experiences in the chemical processing industries provide the background and data base for the formulation and design of a conceptual process for a commercial-scale tire reclamation plant to convert scrap tire feedstock into marketable products (carbon black, oil, and hydrocarbon gases). The process is depicted in a simplified material flow and unit operation sequence in Figure 3.4. The conceptual plant flow sheet is shown as Figure 3.5. A description of the process and of its operation is given in this section.

3.3.1 Tire Receiving and Storage

Tires are received at a loading dock both in bales and loose. Weights are logged in after weighing on a scale of 75-ton capacity. A fork lift

TABLE 3.1. ESTIMATED PRODUCT YIELDS FOR A MOLTEN SALT PYROLYSIS PLANT, BASED ON THE AVERAGE OF FOUR BENCH-SCALE EXPERIMENTAL RUNS

Product	Yield Wt. % of Feed	Annual Yield* lb x 10^{-7}
Hydrocarbon Gases	17.9	0.805
Oil	30.7	1.38
Carbon Black	44.2	1.99
Refuse (Steel wire and Fiberglass)	5.0	0.225
Loss**	2.2	0.099
Total	100.0	4.5

*For a plant processing 22,500 t/yr of tires
**Estimated as 5% of the total carbon black

TABLE 3.2. GAS ANALYSIS AND YIELDS FOR A MOLTEN SALT PYROLYSIS PLANT PROCESSING 22,500 T/YR OF SCRAP TIRES

Component	Annual Yield			Mole Percent of Total Gas*
	lb x 10^{-6}	lb moles x 10^{-4}	SCF x 10^{-7}	
Methane	2.57	16.08	5.77	50.1
Ethylene	1.53	5.46	1.96	17.0
Ethane	1.70	5.68	2.04	17.7
Propylene	0.795	1.89	0.678	5.9
Propane	0.862	1.96	0.704	6.1
Isobutane	0.391	0.674	0.242	2.1
1-Butene	0.198	0.353	0.127	1.1
Total	8.05	32.1	11.5	100.0

*Average of Bench-Scale Runs 18-21.

TABLE 3.3. MAJOR COMPONENT CLASSES IN THE OIL AND THEIR YIELDS, BASED ON BENCH-SCALE RUNS 18-19. ANNUAL YIELDS ARE BASED ON A THROUGHPUT OF 22,500 T/YR OF TIRES

Component	Volume % of Total Oil	Annual Yield, gal
Aromatics (BTX)	27.05	516,000
Olefins	58.85	1,123,000
Paraffins	14.10	269,000
Total	100.00	1,908,000

Density of the oil = 0.87 g/ml = 7.25 lb/gal

TABLE 3.4. ELEMENTAL ANALYSES OF THE OIL AND CARBON BLACK PRODUCTS, FROM RUN NO. 18

Product	Elemental Analysis, Wt %					
	C	H	O	S	N	Cl
Oil	88.20	10.65	-	0.51	0.03	0.39
Carbon Black	87.14	2.28	4.84	2.10	-	0.94

TABLE 3.5. ANALYTICAL TEST RESULTS ON CARBON BLACK FROM SCRAP TIRES, (MCCAFFREY, 1979)

ASTM Iodine No. (mg/g)	155(1)
Dibutyl Phthalate Absorption (DBPA)(cc/100g)	61.2(2)
Nitrogen Surface Area (N_2SA)(m^2/g)	25
Tinting Strength, % ITRB	34.9(3)
Ash, %	12.2
Volatile, %	13.8
Density, lb/ft^3	31.2

(1) Iodine Number Test inaccurate due to high ash. N_2SA value is representative of true surface area.

(2) Modified DBPA Test - not according to ASTM, due to lack of machine response to torque increase as with normal carbon black. Estimated value only.

(3) Tint paste was "gritty".

NOTE: The recovered black was not de-ashed prior to the analysis. The high ash content would tend to increase the density, depress tint and N_2SA.

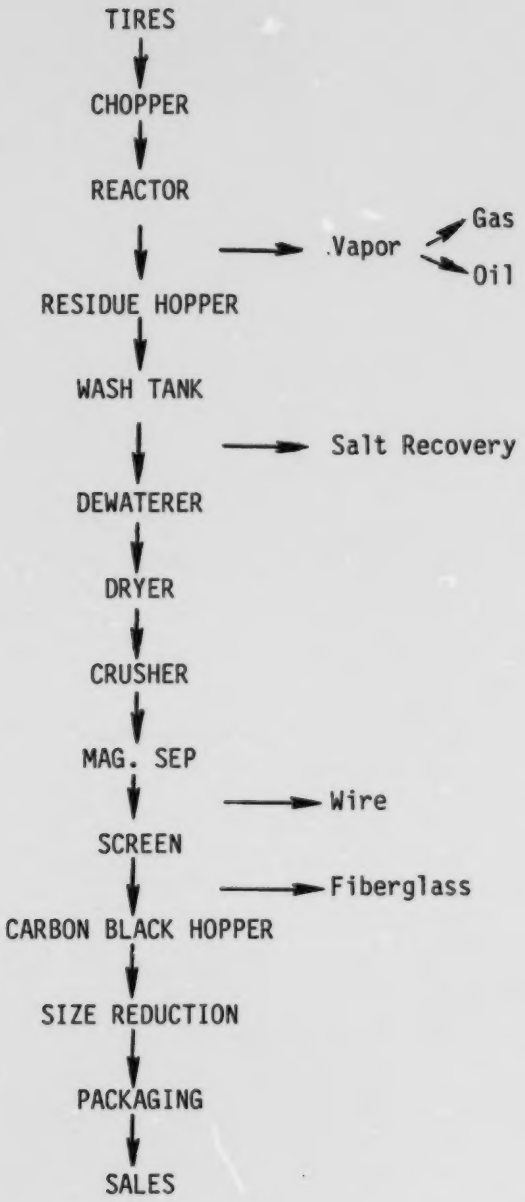


FIGURE 3.4 MATERIAL FLOW AND UNIT OPERATION SEQUENCE

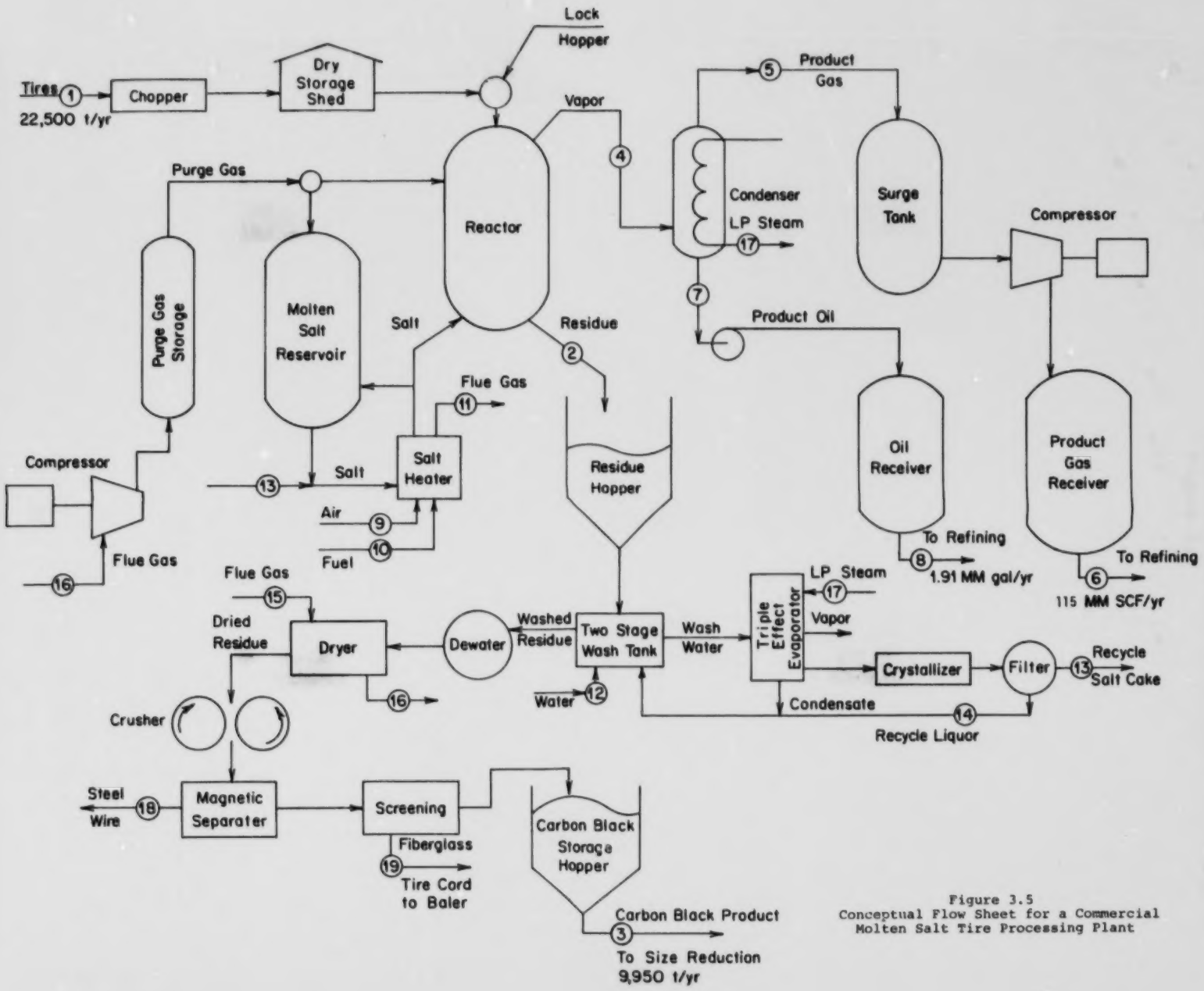


Figure 3.5
Conceptual Flow Sheet for a Commercial Molten Salt Tire Processing Plant

truck is provided for transferring the bales to storage in a dry shed. Tires received wet are chopped and kept in storage until dry in order to minimize corrosion in the reactor that can be accelerated by water. A tire shredder capable of processing 360 auto tires/hr is located in this shed. Such shredders are commercially available. Shredders are also now available which are capable of processing truck tires, but the first unit specified here is for auto tires. The cutting or shredding process not only reduces the volume of the tires, but also helps to eliminate pockets where water might be trapped. Maximum size of the cut tire is about 6" x 20". The shredding operation reduces their volume by 50 to 60 percent. The shredded tires are transported to the reactor by a 24-inch-wide belt conveyor with a capacity of 10 tons/hr.

3.3.2 Reactor

Dry, shredded tires are charged to the reactor through a purged, lock hopper arrangement in order to minimize the introduction of atmospheric air to the reactor. This arrangement is both for safety reasons and for minimizing the production of a corrosive environment within the reactor due to moisture that is normally carried by fresh ambient air.

Each batch of shredded tires charged consists of 4.28 tons, and the batch cycle time is based on 1-1/2 hours. The data upon which these numbers were derived are shown in Tables 3.6 and 3.7.

The reactor I.D. is 8.54 ft, the height 12.0 ft, and the reaction temperature in the range of 715 $\pm$ 36°F (380 $\pm$ 20°C). The height of 12 ft allows for a vapor space above the charge of about 3 ft. The vessel is constructed of 316 stainless steel, after the bench-scale work (see Section 5.0), and the Consolidation Coal Company CSF project work (OCR Report 39, Vol. III, Book 1). That experience indicates the corrosion rate with zinc chloride in the temperature range here (380 $\pm$ 20°C) should be about 70 mil/yr.

Two potential major problems in a batch process involving the transport of molten salt are plugging of lines (due to cold spots) and corrosion of pumps, valves, and fittings. These problems are minimized in the conceptual design, Figure 3.5, by eliminating the need for a salt pump and valves. The salt reservoir, heater, and reactor are also situated in close proximity with one another in order to minimize heat loss from the flow lines.

At the beginning of a reaction cycle, the molten salt is forced by pure gas pressure from the salt reservoir into the reactor. The reactor is located at an elevation of about 10 feet above the salt reservoir so that when the reaction is complete, release of the purge gas pressure over the salt reservoir will allow the salt to drain by gravity back into the reservoir.

The pressure differential between the reactor and reservoir required for the transfer of the salt is about 30 psig. Back pressure in the reactor can

TABLE 3.6. OPERATIONS AND ASSOCIATED TIME PERIODS COMPROMISING THE REACTOR CYCLE

Operation	Time Requirement, minutes
Loading	20
Flooding with Salt	30
Reaction	10
Draining	20
Discharging	10
Total Cycle Time, minutes	90

TABLE 3.7. REACTOR SIZING DATA

Annual Feed Rate, t/yr	22,500.
Daily Feed Rate, tons (90% on-stream factor)	68.5
Batches/day	16.
Charge wt/Batch, tons	4.28
Rubber Density, lb/ft^3	71.7
Shredded Charge Bulk Density, lb/ft^3	20.
Charge Volume, ft^3	428.
Reactor Volume, 20% excess capacity, ft^3 (less vapor space)	514.
Rubber Volume, ft^3	120.
Reactor Free Volume, ft^3 (less vapor space)	394.
Density of Zinc Chloride, lb/ft^3	181.5
Weight Zinc Chloride, with 10% allowance for reactor and head cap and pipes, tons	39.4
Reactor I.D., ft	8.54
Reactor Height, ft	12.00

be as high as 30 psig, due to hydrocarbon gases in the surge tank down stream of the condenser, so the minimum working pressure for the purge gas is about 60 psig. This pressure level also establishes the pressure range within the salt reservoir and in the reactor. That is, the salt reservoir is designed for a working pressure of about 75 psig, and the reactor about 50 psig.

As the rubber density is less than that of the molten salt, tire pieces will tend to float upwards as the salt is forced into the bottom of the reactor. A grid work across the internal section of the reactor, located 3 ft below the reactor head prevents this action, so that a vapor-salt disengaging space is maintained in the top part of the vessel. This zone minimizes the carry-over of salt into the vapor line.

The reactor salt fill time of 30 minutes, Table 3.6, was established with the consideration that large volumes of vapor are generated when the hot salt comes into contact with the rubber. This relatively long fill time was therefore taken to reduce the bumping, splashing, and salt carry-over into the vapor line potentially associated with a reaction of this type. A conductivity probe located within the reactor vessel indicates when the salt level has reached the design fill level, just above the tire level.

The vapor product is piped to a heat exchanger where the oil is condensed out, and where low pressure steam, for use in the salt recovery section, is produced.

After completion of the reaction, which requires about ten minutes at the design temperature of 715 $\pm$ 36^{o}F (380 $\pm$ 20^{o}C), the purge gas pressure is relieved in the salt reservoir, so that the salt drains out of the reactor. The reactor residue, consisting of chunks and particles of carbon black, matted with fiberglass and steel wire, is then dropped into a hopper. The reaction cycle is then repeated.

The purge gas used to force the salt flow and to blanket the reactor during charging is compressed flue gas, which has been cooled by its use in the carbon black dryer. This gas will be deficient in oxygen and will not support combustion when mixed with the hydrocarbon vapors produced in the reactor. Dry purge gas is required to minimize corrosion in both the salt reservoir and in the reactor. Most of the moisture picked up by this gas in the dryer will be condensed out in the purge gas storage tank where the pressure is 100 psig maximum.

3.3.3 Molten Salt Reservoir

The salt reservoir acts as a storage vessel for the salt during the time the reactor is being charged with fresh rubber. The effective volume of this vessel is therefore equal to that of the charge volume of the reactor, plus 20% as a margin of safety. This yields an effective salt reservoir volume essentially equal to the reactor volume: 428 ft^{3}. The dimensions are essentially the same as those of the reactor, 8.54 ft I.D., but only 9 ft in height as a vapor space is not required. A coil is mounted directly within this vessel through which flue gas is circulated in order to heat up the salt

at the system startup and to balance the heat loss from the vessel during operation. Salt also circulates by gravity through the coils of the salt heater. A port is provided for charging the vessel and for adding make-up salt. This vessel is designed for a purge gas pressure of 75 psig so that the salt can be forced against a head of about 20 ft, plus 30 psig reactor back pressure. Appropriate valving cycles the gas pressure, as required for the reactor filling and discharging operations. This vessel is charged with 39.4 tons of zinc chloride salt.

3.3.4 Salt Heater

The salt heater supplies the energy required for heating the system at startup, for balancing the heat losses, and for heating up the reactor charge of rubber from ambient temperature to the reaction temperature of 715 ± 36°F (380 ± 20°C). The heat of reaction for rubber products is expected to be slightly endothermic as is generally the case with hydrocarbon cracking reactions (Melson, 1969).

During steady, cyclic operation of the reactor, the sensible heat required for the rubber tires is expected to be the major heat requirement. Estimated heat loads are tabulated in Table 3.8. The salt heater duty is about 3.80 MM Btu/batch, but this heat is to be supplied in a period of about one hour. A heater duty of 4 MM Btu/hr will satisfy this service with an excess capacity of about 6%. A direct fired heater is specified, with tubes of 316 SS. The flue gas from the heater supplies the energy for drying the carbon black. As this gas is deficient in oxygen, fires should not be produced in the drying operation.

3.3.5 Product Oil and Gas Recovery Train

3.3.5.1 Vapor Cooling and Oil Condensation--

The reactor off-gas consists of hydrocarbon gases and oil vapors as shown in Tables 3.2 and 3.3. In addition a trace quantity of water will be in this vapor. This vapor stream exits the reactor at about 715 ± 36°F (380 ± 20°C). This vapor is produced over a time period of about 40 minutes during each batch cycle of 1-1/2 hours. The average flow rate over the 40-minute gas evolution period is estimated to be about 6.24 M lb/hr.

This stream is cooled in two stages. The first stage generates low pressure steam (25 psig) for use in the evaporators in the salt recovery train. The vapor stream will leave this steam generator at about 285°F (140°C), at which temperature it is estimated that about two-thirds of the oil will have condensed. The vapor stream then enters a water-cooled heat exchanger, where the remaining oil condenses and the entire stream is brought down to 110°F (43°C). The gas passes through a demister to the gas surge tank. The oil is pumped to storage.

The steam generator is sized for a duty of 2.5 MM Btu/hr including a 20% excess capacity factor, but as this heat transfer takes place during only 40 minutes of each 1-1/2 hour batch cycle, the average heat transfer (less the

TABLE 3.8. HEAT REQUIREMENTS FOR THE REACTOR - SALT RESERVOIR SYSTEM

Item	Data/Specifications	Estimated Heat Requirement, Btu/Batch
Reactor Loss	6" Calcium Silicate Insulation k = 0.037 Btu/(hr ft ^{o}F)	38,600
Salt Reservoir Loss	6" Calcium Silicate Insulation k = 0.037 Btu/(hr ft ^{o}F)	28,900
Loss From Piping	~40 ft x 1.40 ft I.D. with 6" Calcium Silicate Insulation k = 0.037 Btu/(hr ft ^{o}F)	11,400
Sensible Heat		
Rubber Tires	4.28 tons/batch, with heat capacity ≃0.48 Btu/(lb ^{o}F)	2,650,000
Purge Gas	~100 scfm, with heat capacity ≃0.25 Btu/(lb ^{o}F)	79,000
Salt	530 lb/batch, heat capacity of solid ≃0.144 Btu/(lb ^{o}F)	62,500
Heat of Reaction, at about 100 Btu/lb		856,000
Heat of Fusion of Makeup (90 lb/batch) plus Recycle Salt (440 lb/batch). Latent Heat = 72.6 Btu/lb		38,500
Total Heat Requirements		3,765,000

20% factor) available for the evaporators is 0.933 MM Btu/hr, which is equivalent to about 1,000 lb of steam/hr.

The second stage condenser is sized for a duty (20% excess capacity) of 1.9 MM Btu/hr.

The data and assumptions used in obtaining these estimates are shown in Table 3.9.

Stainless steel tube and shell exchangers are prescribed for this service, as the oil contains trace quantities of chlorides. Surface areas required for single shell pass designs are:

Steam Generator = 390 ft^2; Second Stage = 490 ft^2

3.3.5.2 Oil Storage--

The oil is pumped directly to storage in a stainless clad vessel of 39,500 gal, a capacity sufficient for about one week's production. Stainless is recommended for this service because of the chloride content of the oil. In special locations (see Maps, Figures 3.2 and 3.3), it may be possible to avoid the cost associated with this storage if the product oil can be pumped directly "over the fence" for purification and separation in existing processing facilities.

3.3.5.3 Product Gas Surge Tank--

The reactor, and hence the vapor train, operates on a batch, or intermittent, basis. The utilization of a surge tank of appropriate size in the product gas line smooths the flow and allows one to size the compressor ahead of the storage tank for average, rather than peak flow, rates.

The gas production data are shown in Table 3.10. Based on a gas volume of about 8.0 Mft^3/batch at 30 psig and 110°F, a surge tank of about 12,000 ft^3 is recommended for this vessel. A check valve upstream of the surge tank prevents reversed flow when the reactor is opened for charging.

The gas is transported by action of the compressor from the surge tank to the gas storage tank.

3.3.5.4 Product Gas Compression--

Storage of large quantities of gases consisting of appreciable fractions of non-condensibles such as methane is generally of doubtful economics. We have, therefore, provided only a bare minimum of gas storage capacity on site, with a tank pressure of 75 psig. The compressor size required for this application can therefore be estimated using the following equation (Peters and Timmerhaus, 1968), and an overall efficiency of 60%:

TABLE 3.9. DATA AND ASSUMPTIONS FOR ESTIMATING THE STEAM GENERATOR AND CONDENSER DUTIES

Mean Heat Capacities, Btu/(lb°F)	
Hydrocarbon Gases *	0.505
Oil Vapor **	0.60
Steam	0.45
Latent Heat of the oil+, Btu/lb	169.
Flow Rates, M lb/Batch	
Hydrocarbon Gases	1.503
Oil Vapor	2.63
Water	0.50
Temperature Let Down, °F	
Steam Generator	715-285
Condenser	285-110

* Average of the major components, methane, ethane, and ethylene
** Estimated
\+ Not known, but estimated to be similar to benzene

TABLE 3.10. HYDROCARBON GAS PRODUCTION DATA FOR TANK AND COMPRESSOR SIZING

Gas Average Molecule Weight, lb/lb mole	25.6
Gas Production,	
M lb/Batch	1.503
Mscf/Batch	21.0
Gas Volume at 30 psig and 110°F,	
Mft^3/Batch	8.0
Flow Rates:	
Maximum, Mscfm	525.
Average, Mscfm	234.

Data for use in computing the compressor size are shown in Table 3.11. Heat capacity ratios are provided for the major components in the gas only. The use of the value for methane yields a slightly larger power requirement than for the other components, and since methane is the largest fraction in the gas, the compressor is sized using k = 1.31. The power requirement so determined is 65 hp, using a 60% overall compression efficiency.

3.3.5.5 Product Gas Storage--

Product gas is stored in a 12,000 ft^3 carbon steel, spherical vessel at 75 psig. This volume is sufficient for storage of the gas from only about four batches of tires (1/4 day's production). This means the gas must be piped more or less as generated "over the fence" to market, or used on site (for firing the salt heater, for example). The gas contains appreciable portions of olefins, so its value as chemical feedstock is greater than as fuel, if established "over the fence" facilities are available for purification. If such facilities are available, it may be possible to eliminate the gas storage tank at an appreciable savings of capital investment.

3.3.6 Reactor Discharging and Residue Hopper

After the completion of a reaction cycle, the salt is allowed to drain by gravity into the salt reservoir, after which the residue is dropped from the reactor into a stainless holding hopper of 760 ft^3 capacity. This residue will consist of raw carbon black, fiberglass, steel wire, and trace quantities of zinc chloride salt which cling to the solids. The weight of a residue batch including salt is estimated to be about 4,843 lb, with the estimated composition shown in Table 3.12. The task is to recover the carbon black and the salt in relatively pure form. Two processing trains are therefore provided at this point: one to wash, dry, and separate the fibers and wire from the carbon black, and the other to recover the salt from the carbon black wash water, for recycle to the salt reservoir.

3.3.7 Carbon Black Recovery Train

Bench-scale experimental results obtained using 12-inch strips of rubber cut from scrap tires indicated the reactor residue to be a dry, hard, friable product. Carbon particles would fall readily from the mat, leaving a free fiberglass "fluff" with a minimum of crushing required in order to free the fibers from the carbon. Organic fibers such as polyester, which may be present in the rubber, were completely pyrolyzed leaving voids within the carbon matrix.

However, there are trace quantities of salt on the residue when it emerges from the reactor, most of which can be removed by washing in water. It is not known at this point how much the salt carry-over would be in a commercial reactor, but a reasonable estimate is a maximum of about 0.1 lb salt/lb salt-free residue. The task at this point is to wash the residue free of salt, separate out the fibers and steel wire, and recover the salt from the wash water.

TABLE 3.11. DATA USED FOR SIZING THE PRODUCT GAS COMPRESSOR

Pressures: Inlet, P_1	14.7 psia
Outlet, P_2	89.7 psia
Volumetric Flow Rate, Q_1, at 110°F and 14.7 psia:	271 cfm
Heat Capacity Ratios (C_p/C_v)*, k:	
Methane	1.31
Ethylene	1.26
Ethane	1.22

* From Perry's Handbook, 5th Ed, Table 3-181

TABLE 3.12. ESTIMATED COMPOSITION AND QUANTITIES OF RESIDUE FROM THE REACTOR, PER BATCH, FOR A PLANT PROCESSING 22,500 T/Y OF TIRES

Component	Amount, lb	Avg. Flow Rate, lb/hr	Weight, %
Carbon Black	3,975	2,650	82.1
Steel Wire*	232	155	4.8
Fiberglass*	196	131	4.0
Zinc Chloride **	440	293	9.1
TOTAL	4,843	3,229	100.

*Proportions from Gains and Wolsky (1979).
**Estimated as 0.1 lb salt/lb residue.

3.3.7.1 Residue Wash Tank--

Under steady operating conditions the residue would be dropped hot into the first stage of a two-stage wash tank. The heat of the carbon residue will therefore be used to heat the first-stage wash water to near the boiling point. The wash water consists of recycle liquor (from salt recovery) and condensate from the evaporator. It is estimated that this stage will remove a minimum of 90 percent of the recoverable chlorides from the residue. The second-stage wash, with fresh make-up water, will remove about 90 percent of the remaining recoverable salt, for a total salt extraction of 99+ percent.

The wash tank is sized to hold two batches of residue with a bulk volume of about 240 ft^3 per batch. One batch is in the first-stage wash, the other in the second. A tank of 4500-gal capacity will meet this requirement.

Experience with residue solids of this physical type is not available at this time, so the water content of the wet residue is unknown. It is expected, however, to be greater than 0.25 lb water/lb solids. If such is the case, this is more water than can be evaporated with the available flue gas from the salt heater, so a stainless, centrifugal dewaterer is provided upstream of the dryer, as depicted in Figure 3.5. The solids are transported from the wash tank to the dewaterer by a belt conveyor.

3.3.7.2 Residue Dewatering--

The residue is dewatered in order to limit the evaporative load in the dryer. Dewatering also removes water which contains trace amounts of chlorides and therefore improves product quality.

The solid material to be dewatered consists of about 4,400 lb/batch, with one batch every 1-1/2 hours. The volume of the material per batch is expected to be not more than about 240 ft^3. The solids volumetric flow rate to the dewaterer is therefore expected to be not more than about 3.0 cfm. A centrifugal filter with a bowl size of 36 inches should accommodate this throughput rate. The solids leave the dewaterer with a water content of less than 0.25 lb/lb solids.

3.3.7.3 Residue Dryer--

The dewatered solids are conveyed to a rotary dryer where the moisture is evaporated by direct contact with the flue gas from the salt heater. This gas is deficient in oxygen, so there is little, if any, danger of dust fires or explosions.

The average flow rate of solids to the dryer is about 4,400 lb each 1-1/2 hours, or about 2,930 lb/hr. With a maximum water content of 0.25 lb water/lb solids, the maximum evaporative load is about 733 lb water/hr. These and other data required for sizing the dryer are shown in Table 3.13. The size of the countercurrent rotary dryer was estimated using (Perry's Handbook):

$$Q = 0.4LD\ G^{.67}\ \Delta T_{ln}$$

TABLE 3.13. DATA USED IN SIZING THE RESIDUE DRYER

Temperatures		
Flue Gas in		780°F
out		240°F
Solids in		180°F
out		215°F
Flow Rates		
Solids, lb/hr	2,930	
Water, lb/hr	733	
Flue Gas, lb/hr	4,850	
Thermal Load		
Sensible heat, solids, Btu/hr	51,300	
Sensible heat, water, Btu/hr	23,500	
Latent heat, water, Btu/hr	711,000	
Total thermal load, Q, Btu/hr	786,000	

This calculation yields a diameter of 5 ft and a length of 43 ft, for a surface of 675 ft^2.

Part of the flue gas from the dryer is directed to the purge gas compressor. The solids are conveyed to the residue crusher.

3.3.7.4 Residue Crushing--

The dried residue is a mixture of carbon, fiberglass and steel wire. The handling operations up to this point will have broken up much of the carbon, releasing some of the fiberglass tire cord and wire. However, it is anticipated that some of the fiberglass and carbon will still exist in the form of a mat, and require a mild crushing so that the carbon can fall away from the fiberglass and wire matrix.

The capacity required of the crusher is about 2930 lb/hr, rounded to 1-1/2 ton/hr. The smallest roll crusher available, about 24" x 14", will be more than adequate for this application.

The crushed mixture is next transported by conveyer to the magnetic separater.

3.3.7.5 Magnetic Separater--

The steel wire pieces, estimated to be 3-18 inches in length, are separated from the residue mixture by a magnetic rotary drum device.

The feed to the magnetic separator consists of about 2,650, 130, and 155 lb/hr, respectively, of carbon, fiberglass, and steel wire. The separated scrap wire may have value for applications such as concrete reinforcing or as foundry feedstock. However, no value has been assigned to this material in this analysis.

The carbon particles and fiberglass fall from the crusher into the feed chute of the screen.

3.3.7.6 Screening--

The fiberglass, in the form of individual fibers and mat, from about 3 inches to 18 inches in length, is separated from the carbon particles by a screening-type operation. Top size of the carbon particles at this point is estimated to be about 3/8 inch. The separation operation is more in the nature of "trash removal" or "scalping" than solids classification, with about 130 lb of fiberglass to be removed from 2,630 lb of carbon particles per hour.

Factors taken into consideration in the selection of the type of screening device for this application are the need to separate and move the fibers to a baler, and the need to minimize the production of dust. An enclosed, inclined, vibrating, two-stage screen is recommended for this application, although such a device should be tested at the pilot plant scale before the process design of a commercial plant is finalized.

The fiberglass refuse is conveyed to a baler. No value is assigned to this product. The carbon black is conveyed to a storage hopper.

3.3.7.7 Residue Hopper--

The carbon black is stored in a hopper of 2,000 ft^3 capacity, prior to bagging and shipment. The bulk density of the material is estimated to be 31 lb/ft^3 and the average flow rate is 2,630 lb/hr. Approximately one day's production can be stored in this facility.

3.3.7.8 Additional Carbon Black Processing--

The raw carbon black at this stage consists of particles 0 x 3/8 inch. The minimum processing required in order for this material to meet existing carbon black specifications is grinding to a top size of the order of 1.0 μm or less. It is not known what additional processing may be required, as sufficient quantities of this material have not been produced for test compounding into products such as ink, plastics, or rubber. As a consequence, the type or grade of carbon black which can be produced by molten salt pyrolysis of rubber is not known at this time. The product material from the conceptual process design is considered to be raw stock material and is assigned a value as described in Section 5.0, Economic Evaluation and Assessment.

3.3.7.9 Figberglass Baling--

The fiberglass separated from the carbon black stream is a light, fluffy matrix, and is baled to facilitate transport and disposal in a landfill. This material amounts to about 130 lb/hr.

3.3.8 Zinc Chloride Salt Recovery Train

The salt which clings to the reactor residue is washed from the solids as described in Section 3.3.7.1. The salty wash water is processed in this section of the plant to recover the salt for two reasons: discard of this salt would be of doubtful economics; and discharge of this quantity of zinc chloride to the sewer would probably not be environmentally acceptable. The salt recovery train is therefore designed to separate out this salt for recycle to the molten salt reservoir.

The sizing of this section of the plant depends mainly on the quantity of salt carried out of the reactor on the carbon residue. Experimental data are not available for the quantity of salt carried with the residue*. It has been necessary to estimate the salt content of the residue so the sizing of the salt recovery train presented here and the associated economics of salt recovery presented in Section 4.0 must be considered approximate at this time. Operation of the process at the pilot scale is recommended prior to finalization of a commercial plant design, in order to firm up these and other estimates.

*Our bench-scale data are not considered reliable for estimating purposes, due to such factors as residue shape, size, and method of reactor discharge.

Trace quantities of carbon black particles will also be carried with the wash water through the salt recovery train. Most of these particles will be recovered on the filter along with the salt crystals. The salt recycled to the process will therefore be a mixture of carbon particles and zinc chloride. However, bench-scale results using such mixtures in the recycle do not indicate any loss of effectiveness of the molten salt in promoting the pyrolysis reaction.

Some carbon particles may pass through the filter, and be recycled to the wash tank with the recycle liquor. The process thus avoids the problem of having to treat "black water" for discharge to the drain.

3.3.8.1 Evaporation--

The salty wash water is pumped to a triple-effect evaporator where the salt is concentrated by the use of LP steam produced in the product vapor cooling and condensing section. This water will contain 5 - 10 wt% salt on the average, and the flow rate will be about 5,000 lb/hr. The water will also carry trace quantities of carbon particles.

An important parameter establishing the quantity of wash water required is the bulk density of the residue, and the free (void) volume within the material, as the batch of residue is flooded with water in the washing process. It is assumed here, as the residue is easily broken and compacted, that the solids volume in the wash tank is only about 28 percent of the original tire volume, corresponding to a void (free) volume of about 50 percent. With this assumption, the data shown in Table 3.14, and the zinc chloride solubility data contained in the Appendix, the LP steam requirement for the triple-effect evaporator is estimated to be about 1,780 lb/hr. This quantity is somewhat greater than the estimated production of steam in the vapor condenser, so it may be necessary to provide facilities for recovery of heat from the hot residue and from the flue gas exiting the dryer, for a second LP steam generator in the vapor condensation train, or for heat exchange against the hot liquor leaving the evaporator.

The enthalpy of zinc chloride-water solutions apparently is not available, so the heat of vaporization of the salt solutions was approximated as that of water alone. With these assumptions, the total area required for the triple-effect evaporator is estimated to be about 1,350 ft^2.

3.3.8.2 Salt Crystallization--

The concentrated salt solution leaves the evaporator at about 230°F, with a salt weight fraction of about 0.75. The flow rate is about 590 lb/hr. The salt flow through the unit consists of a recycle portion, about 150 lb/hr, and a fresh feed portion of about 290 lb/hr. This stream cools in a holding tank just prior to the crystallizer to about 160°F. It is then fed into a vacuum, batch crystallizer whose capacity is 200 gal. Construction is rubber-lined steel.

The crystal-liquor slurry is pumped to the filtration unit.

TABLE 3.14. DATA USED IN COMPUTATION OF THE EVAPORATOR DUTY AND IN SIZING THE EVAPORATOR

Bulk Volume of Residue, ft^3/batch	240.
Residue Void Fraction	0.5
Wash Water/Batch, lb	7,500.
Salt Content of Wash Water, wt%	8.
Salt Content of Liquor from Evaporator, wt%	75.
Average Wash Water Flow Rate, lb/hr	5,000.
Average Evaporation Rate, lb/hr	4,450.
Supply Steam Rate, lb/hr	1,780.
Average Overall Heat Transfer Coefficient, U, Btu/(hr ft^2)	80.

3.3.8.3 Salt Filtration--

The salt crystals and trace quantities of carbon particles are separated from the salt liquor by a continuous, vacuum drum rotary filter. Construction is of stainless steel. The outlet streams consist of about 290 lb/hr (dry weight) of wet crystals, and about 300 lb/hr salt liquor containing about 50 percent salt. The salt crystals are conveyed to a dryer before being recycled to the salt reservoir. The salt liquor is recycled to the first stage of the residue wash tank after being diluted with condensate.

3.3.8.4 Salt Drying--

Before recycle to the salt reservoir, the salt is dried in a vacuum drum dryer, which has a capacity of 300 lb/hr of dry cake.

3.3.9 Purge Gas Compression

Purge gas is used to blanket the reactor during charging operations and to force the molten salt from the reservoir into the reactor. A portion of the flue gas exiting the dryer is used for this purpose. This gas is deficient in oxygen and spontaneous ignition will not occur when this gas is mixed with hydrocarbon vapor and gases in the temperature range (~4000°C) encountered in the reactor. Capacity is provided for compressing 200 scfm of this gas.

This gas, as received at the compressor, will contain considerable moisture. However, when it is compressed to the storage tank pressure of 100 psig, most of this moisture will condense out as the gas cools. The water vapor in the cooled gas should not be more than about 0.4 percent. Although this gas also contains several percent CO_2, its major constituent is

nitrogen. The heat capacity ratio of nitrogen is therefore used in estimating the power required for compression. The power requirement, with an overall efficiency of 60 percent, is estimated to be 60 hp.

3.3.10 Purge Gas Storage

Purge gas storage is in a 5 ft i.d. x 12.5 ft, horizontal, cylindrical steel vessel. At a maximum pressure of 100 psig, the vessel provides a purge gas capacity of about 1700 scf.

3.3.11 Additional Equipment

In addition to the major components described in the preceding Sections, some additional major support items required at the plant are weight scales for the scrap rubber tires, hoist, fuel oil storage, a fork lift for moving the tires, and conveyors at various locations in the process trains.

3.3.12 Summary of Major Process Equipment

The major components required in the process conceptual design are summarized in Table 3.15, along with the estimated size requirements for a 22,500 t/yr plant. These requirements form the basis of the process economic assessment summarized in Section 4.0.

TABLE 3.15 SUMMARY OF MAJOR PROCESS EQUIPMENT COMPONENTS

Item	Description	Size/Amount	Design Pressure/Temperature
Molten Salt Reservoir	Cylindrical, Vertical, 316 ss	8.54 ft i.d. x 9.00 ft high	75 psig; 400°C Wall
Reactor Vessel	Cylindrical, Vertical, 316 ss	8.54 ft i.d. x 12.00 ft high	30 psig; 400°C Wall
Salt Heater	Direct Fired, 316 ss Tubes	4.0 MM Btu/hr	75 psig; 425°C Wall
Heat Exchangers			
L.P. Steam Gen.	Tube and Shell, 316 ss	2.5 MM Btu/hr, 390 ft^2	30 psig; 380 $\pm$ 20°C
Condenser, Vapor	Tube and Shell Water Cooled, 316 ss	1.9 MM Btu/hr, 490 ft^2	30 psig; 380 $\pm$ 20°C
Gas Surge Tank	Spherical, cs	12,000 ft^3	30 psig; Ambient
Gas Storage Tank	Spherical, cs	12,000 ft^3	75 psig; Ambient
Product Oil Storage Tank	Cylindrical, ss	39,500 gal	Ambient
Pump, Product Oil	Centrifugal, ss	4 gal/min, 60-ft Head	Ambient
Purge Gas Storage Tank	Cylindrical, cs	5 ft I.D, x 12.5 ft 245 ft^3	100 psig; Ambient
Purge Gas Compressor	Single Stage, Double Acting	200 scfm; 60 hp	100 psig, Ambient
Product Gas Compressor	Single Stage, Double Acting	275 scfm; 60 hp	75 psig; Ambient
Residue Hopper	Conical, ss	760 ft^3	Abmient; 380°C
Carbon Black Hopper	Conical, cs	2,000 ft^3	Ambient
Residue Wash Tank	ss	5,800 gal	Ambient; 100°C
Centrifugal Separator, w/Motor	ss	36-inch bowl	Ambient; 100°C

TABLE 3.15 (Continued)

Item	Description	Size/Amount	Design Pressure/Temperature
Dryer, Residue	Rotary, Direct Flue Gas	0.8 MM Btu/hr, 5 ft x 43 ft	
Crusher, Residue	Roll	3,000 lb/hr, 24 inch x 14 inch	
Magnet Separator Wire	Rotary Drum	155 lb/hr, wire pieces	
Screen Residue	Enclosed, inclined, vibrating, two-stage		
Evaporator, Wash Water	Tripple Effect, Verticle Tube, CI body, ss tubes	1,340 ft^2	Vac.; 268°F
Crystallizer, Salt Recovery	Vacuum, Rubber Lined	200 gal	Vac.
Filter, Salt Recovery	Vacuum Drum, ss	20 ft^2	
Dryer, Salt Cake	Vacuum Drum, ss	75 ft^2	
Tire Chopper		360 tires/hr	
Baler, Fiberglass		130 lb/hr	
Tire Feed Conveyer	Belt Type	18 in x 50 ft	
Conveyors, Carbon Black Train	Belt Type	16 in x 200 ft	
Hoist, Storage Shed	Electric, with Trolley	2.0 tons	
Hoist, Reactor Vessel Port	Electric	1.0 ton	
Fork Lift	72 inch lift	4,000 lb	
Weigh Scales, Carbon Black		1,000 lb	
Weigh Scales, Tire Receiving		75 tons	

4.0 ECONOMIC EVALUATION AND ASSESSMENT

The economic evaluation presented here is in terms of return on investment (ROI) for a plant sized to process 22,500 t/yr of scrap auto tires, in terms of late 1979 dollars. Required for this assessment are total capital requirements, financing arrangements, plant write-off period wage rates, cost of raw materials (scrap tires), and selling prices for the products.

The method fo computing total capital requirements used here follows that of Peters and Timmerhaus (1968), which is based upon estimating the plant physical and indirect cost using pre-established ratios and the total cost of the major process equipment components, in terms of base-year dollars (1967 in this case).

The total fixed capital requirements are then brought forward (to late 1979 dollars) using an appropriate inflationary index, such as the Marshall and Stevens (M&S) Chemical Process Industries Cost Index.

Our initial analysis based on the sale of all products from the tires for fuel indicated there is little possibility (short of a "negative" scrap tire feed cost) a plant of this type could be profitable with energy prices in the range of 3-5 $/MM Btu. We therefore considered recovery (and marketability at late 1979 prices) of the major product components having value as chemical feed stocks: carbon black, olefin gases, and the aromatic oils (BTX). The oil and gas remaining in the product streams were assigned fuel values. The fiberglass and steel wire refuse were assigned no value, although the latter might be worth as much as $24,500 per year, priced at 40 $/t.

The details of our evaluation follow.

4.1 PROCESS EQUIPMENT COSTS

The process equipment components listed in Table 3.15 were costed (1967 basis) using data and curves provided by Peters and Timmerhaus (1968), by Guthrie (1969), and in certain cases, quotations from vendors. The equipment cost values arrived at, and used, in this assessment are summarized in Table 4.1. Total major equipment delivered cost is estimated at $513,000, early 1967 basis. The M&S Chemical Process Industries Cost Index for January 1967 was 256 (see Perry's Handbook, for example), and 622.9 for the fourth quarter, 1979 (Chemical Engineering, March 10, 1980). The estimated process equipment cost (E) in late 1979 dollars is therefore:

TABLE 4.1. SUMMARY OF ESTIMATED PROCESS EQUIPMENT COSTS

Item	Size/Amount	Estimated Costs, $, Jan. 1967, FOB	Delivered*	Reference
Molten Salt Reservoir	8.54 ft i.d. x 9.00 ft, ss	27,800	30,000	Guthrie
Reactor Vessel	8.54 ft i.d. x 12.00 ft, ss	26,500	28,600	Guthrie
Lock Hopper	500 ft^3, cs		8,000	Estimated
Salt Heater	4 MM Btu/hr, ss	27,000	29,200	Guthrie
L P Steam Generator	390 ft^2, ss	12,250	13,200	Guthrie
Condenser, Vapor	490 ft^2, ss	14,250	15,400	Guthrie
Gas Surge Tank	12,000 ft^3, cs	45,000	48,600	P & T(1)
Gas Storage Tank	12,000 ft^3, cs	45,000	48,600	P & T
Product Oil Storage Tank	39,500 gal, ss	20,700	22,400	P & T, with 2.25 Stainless Factor
Pump, Product Oil	4 gal/min, 60 ft head, ss	600	650	P & T, with 1.8 Stainless Factor
Purge Gas Storage Tank	245 ft^3, 100 psig, cs	2,800	3,000	Guthrie
Purge Gas Compressor with Motor	200 cfm	14,000	15,100	P & T
Product Gas Compressor with Motor	275 cfm	17,000	18,400	P & T
Residue Hopper	760 ft^3, ss	200	220	Guthrie
Carbon Black Hopper	2,000 ft^3, cs	200	220	Guthrie
Residue Wash Tank	4,500 gal, ss	9,500	10,300	P & T
Centrifugal Separator, with Motor	40-inch bowl, ss	34,000	36,700	P & T
Dryer, Rotary Direct	675 ft^2	43,400	46,900	P & T
Crusher, Residue, with Motor	24 inch x 14 inch	6,000	6,500	P & T

TABLE 4.1. (Continued)

Item	Size/Amount	Estimated Costs, $, Jan. 1967, FOB	Delivered*	Reference
Magnetic Separator	155 lb/hr		5,000	Estimate
Screen, Residue, inclined vibrating, doubledeck	20 ft^2, 3/8-inch top size		2,100	P & T
Evaporator, Wash Water	1350 ft^2, CI		36,900	P & T
Crystallizer, Salt Recovery	200 gal		9,000	P & T
Filter, Salt Recovery Complete Unit	20 ft^2	17,000	18,400	P & T
Dryer, Salt Cake, Vacuum	75 ft^2, ss		7,600	P & T
Tire Chopper	360 tires/hr		14,700	Est., Nat'l Std. Co.
Baler, Fiberglass	~130 lb/hr		6,000	Estimated
Tire Feed Conveyor	18 inch x 50 ft	3,600	3,900	P & T
Conveyor, Belt, Carbon Black Train	16 inch x 200 ft	5,800	6,300	P & T
Hoist, Storage Shed	2.0 tons	3,000	3,200	P & T
Hoist, Reactor Vessel Opening	1.0 ton	1,000	1,080	P & T
Fork Lift	72 inch, 4000 lb		7,100	P & T
Weigh Scales	1,000 lb		1,500	Guthrie
Weigh Scales	75 ton		8,500	Guthrie
Zinc Chloride Salt	39.4 tons	$42/100 lb	38,700	CMR, 10 Dec. 1979
Total Estimated Process Equipment Costs = (excluding salt)			$ 513,300	

*Delivery Costs were computed as 1.08 times FOB cost, when not available.

(1) P & T = Peters and Timmerhaus

$$E = \$513,270 \times \frac{622.8}{256} = \underline{\underline{\$1,248,000}}$$

This estimated cost is used to compute the Total Fixed Capital Requirements as explained in the following section. Major items in this cost are the product oil and gas storage facilities, which amount to 13.8 percent of the total major equipment costs. A substantial reduction in capital requirements can therefore be achieved for those installations where the product gas and oil can be piped directly to the customer without holdup.

4.2 PLANT CAPITAL COST

Mid-range values of factors for costs on items such as installation, etc., were taken from Peters and Timmerhaus as being representative for this plant. The cost of the initial charge of zinc chloride, estimated as 39.4 tons at $42/100 lb (CMR Dec. 10, 1979) with an estimated 8 percent delivery cost, is also capitalized. The estimated capital requirements, as shown in Table 4.2, amount to a total of $5,772,000. This value includes construction interest at 10 percent with a linear capital drawdown over a 12-month construction period.

4.3 ANNUAL OPERATING COSTS

Most of the operating costs can be estimated using established ratios for the chemical processing industry. However, there are two costs associated with this process about which there is considerable uncertainty at this time. These are the cost of the feed material, the scrap tires, and also the cost of separating and purifying the chemicals, such as olefin gases and BTX liquids from the product gas and liquid streams. We therefore estimated a range for each of these two costs, based upon partial data in the literature and upon past experiences in the process industries. We treated these costs as parameters in their respective ranges.

The range taken in this study for the tire cost is 0-40 $/ton. Prices at the low end of this range have been reported in some areas (Laurin, 1980), but in the long run, after the current scrap surplus is consumed, the prices will tend to rise. Values as high as about $40/t have been mentioned in the literature (Berry, 1979).

The chemicals purification cost range is taken as 30-90 percent of the chemical's value. Actual costs will depend on local arrangements with established petroleum refineries and ethylene plants.

The total annual operating cost is computed as the sum of three contributory factors:

TABLE 4.2. FIXED CAPITAL REQUIREMENTS FOR A MOLTEN SALT PYROLYSIS PLANT PROCESSING 22,500 T/YR OF TIRES, IN LATE 1979 DOLLARS

A.	Plant Physical Costs	
	Process Equipment, Delivered (E)	$ 1,248,000
	Installation (.45E)	561,600
	Insulation (.08E)	99,800
	Instrumentation (.18E)	224,600
	Piping (.25E)	312,000
	Electrical (.125E)	156,000
	Buildings (.5E)	674,000
	Site with improvements (.14E)	174,000
	Auxiliaries (.4E)	499,000
	Plant Physical Cost (P)	$ 1,248,000
B.	Indirect Costs	
	Engineering and Construction (.15P)	584,000
	Contractors Fee (.1P)	389,900
	Contingencies (.15P)	584,800
	Total Indirect Costs	$ 1,560,000
C.	Initial Charge of Zinc Chloride (C)	38,700
D.	Construction Interest 0.10(P+I+C)/Z (CI)	274,600
E.	Plant Capital Cost (P+I+C+CI)	$ 5,772,000

- "Base" costs, as summarized in Table 4.3.
- Tire Feed Costs, parameterized in the range of 0-40 $/ton.
- Chemicals purification, 30 - 90 percent of their value.

The base operating costs, Table 4.3, include interest at 10 percent of fixed plus working capital, with working capital taken as 20 percent of fixed capital (from Table 4.2). Depreciation is taken over 8 years for this "environmental" project. Other percentages in Table 4.3 are based on averages for the chemical process industries (Peters and Timmerhaus, 1968).

4.4 REVENUES FROM SALES

The products from the molten-salt-pyrolysis-of-tires process are listed in Tables 3.1 to 3.3. For revenue estimating purposes, we consider these products as consisting of three classes: fuels, chemical feed stocks, and carbon black. The fuels are the paraffinic gases (methane, ethane, propane, and isobutane) and the olefinic and paraffinic liquids. The chemical feed stocks are the olefinic gases (ethylene, propylene, and 1-butene) and the aromatic liquids (principally benzene, toluene and xylene, designated BTX).

The costs of fuels have been changing rapidly in recent years. We have therefore considered the fuel value of the products to be a parameter in this study, in the range of 3 to 5 $/MM Btu. The yields of the fuel products along with their estimated values as fuels are shown in Tables 4.4, 4.5 and 4.6.

The yields and estimated values of the olefinic gases (late 1979 prices) are shown in Table 4.7. As these gases must be separated from the fuel gases, the revenue from these products will be estimated by discounting their values by 30 - 90 percent as a "purification" cost.

The values of the aromatic oils (BTX) are also shown in Table 4.7. The average price of $1.40/gal for this oil was arrived at by averaging the high and low values of benzene, toluene, and xylene in Chemical Marketing Reporter, 10 December 1979, each weighted equally.

The value of the carbon black product is the greatest uncertainty in our economic evaluation at this time, as a sufficient quantity has not been produced for test marketing. We assume here that this product will be marketable after sufficient grinding, and estimate its value in the range of $.15 - $.21/lb. This range was arrived at by discounting the CMR quotations (10 December 1979) of about $.19 to $.28/lb for grinding and for uncertainty as to type, quality, and marketability. The yield-assumed revenues for the carbon black are shown in Table 4.8 for three prices, $.15, $.18, and $.21/lb.

4.5 RETURN ON INVESTMENT

The plant profitability as Return on Investment (ROI) can now be computed. The required economic data are summarized in Table 4.9. A number

TABLE 4.3. ESTIMATED ANNUAL BASE OPERATING COSTS FOR A 22,500 T/YR MSP PLANT

A.	Labor and Supervision (15% of Base Op. Costs) (Salaries and Wages)	$ 591,000
B.	Plant Overhead (60% of Salaries and Wages)	355,000
C.	Utilities (17.5% of Base Op. Costs)	689,000
D.	Chemicals, Makeup Zinc Chloride (4.71×10^5 lb/yr at 42¢/yr	197,800
E.	Insurance (1% of Fixed Capital)	57,600
F.	Taxes (3% of Fixed Capital)	173,000
G.	Maintenance (7% of Fixed Capital)	404,000
H.	Operating Supplies (15% of Maintenance)	60,600
I.	Depreciation (8 yr St. line)	721,000
J.	Interest (10% of Fixed + Working Capital)	692,000
	Base Operating Costs	$ 3,941,000

TABLE 4.4. HEATING VALUE OF THE FUEL GASES FROM A MSP PLANT PROCESSING 22,500 T/YR OF SCRAP TIRES

Component	Annual Yield, lb moles $\times 10^{+4}$	$-\Delta H_{C298}$, Btu/lb mole	Heating Value, Btu/yr $\times 10^{+10}$
Methane	16.08	383,000	6.15
Ethane	5.68	671,000	3.81
Propane	1.96	955,000	1.87
Isobutane	0.674	1,238,000*	0.83
Total			12.66

*Assumed same as n - butane

TABLE 4.5. HEATING VALUE OF THE OIL FUEL COMPONENTS FROM A MSP PLANT PROCESSING 22,500 T/YR OF SCRAP TIRES

Component	Annual Yield, gal x 10^{-6}	Heating Value*, Btu/gal	Heating Value, Btu/yr x 10^{-10}
Olefins + Paraffins	1.392	140,000	19.5

*Perry's Handbook, 4th Edition

TABLE 4.6. ANNUAL REVENUES FROM FUEL PRODUCTS, WITH ENERGY PRICES IN THE RANGE OF 3-5 $/MM BTU

Fuel Product	Annual Revenues, MM $/Yr		
	3 $/MM Btu	4 $/MM Btu	5 $/MM Btu
Gases	0.38	0.506	0.63
Oil	0.585	0.78	0.975
TOTAL	0.965	1.29	1.61

TABLE 4.7. YIELDS AND VALUES OF THE CHEMICAL FEED STOCKS FROM A MSP PLANT PROCESSING 22,500 T/YR OF SCRAP TIRES

Component	Annual Yield* x 10^{-6}	Price**	Value, MM $/Yr
Ethylene	1.53	0.168	0.257
Propylene	0.795	0.148	0.118
1-Butene	0.198	0.185	0.037
Aromatic Oil (BTX)	0.516	1.40	0.722
Total			1.134

* Units are lb/yr for the gases, gal/yr for the oil.
** Units are $/lb for the gases, $/gal for the oil. Values shown are averages of the high and low values in CMR, 10 December 1979.

TABLE 4.8. ANNUAL REVENUE FOR THE CARBON BLACK, AT SALES PRICES OF 15, 18, AND 21 /LB

Product	Annual Yield, lb x 10^{-7}	Revenue, MM $		
		15¢/lb	18¢/lb	21¢/lb
Carbon Black	1.99	2.99	3.58	4.18

TABLE 4.9. SUMMARY OF ECONOMIC DATA ON MM $/YR BASIS FOR A MSP PLANT PROCESSING 22,500 T/YR OF TIRES

A. Fixed Capital, FC				$ 5.772
B. Total Investment (1.2 FC), TI				6.930
C. Revenues:				
Chemicals (Olefin Gases + BTX), CR				1.134
Fuels, FR, at	3$/MM Btu	4$/MM Btu	5$/MM Btu	
	.965	1.29	1.61	
Carbon Black, CBR, at	15¢/lb	18¢/lb	21¢/lb	
	2.99	3.58	4.18	
Total Revenues, TR = CR + FR + CBR				
D. Costs				
Base Operating Costs, BOC				1.134
Tire Feed Costs, TFC, at	0$/t	20$/t	40$/t	
	0.0	0.45	0.90	
Purification Costs, PC	.3 CR	.6 CR	.9 CR	
	.34	.68	1.021	
Total Operating Costs, TOC = BOC + TFC + PC				
Sales, Administration and Research, SAR				0.1TR
Total Annual Costs, TAC = TOC + SAR				

of realistic cases were considered, over the range in cost and revenue parameters shown in Table 4.9. A typical cash analysis sheet is shown as Table 4.10, where, for the values of parameters used, the ROI is 5.34 percent. The complete economic analysis is summarized by the curves shown in Figure 4.1, where the values of the parameters required to produce profit are clearly evident. Generally speaking, it can be seen that for fuel prices in the range of 3-5¢/MM Btu and for carbon black from this process valued in the range of $.15 - $.21/lb, tires must be available at little or no cost in order for a plant of this size (22,500 t/yr of tires) to be profitable. Even so, it appears the profit potential is such, with current fuel and chemical prices, the current tax structure (46 percent of gross profit), and the current interest rates, that it is questionable as to whether a plant of this type and size would attract venture capital. Changing market conditions, and/or tax and interest rates could change this picture. However, alternatives such as other competing processes and restrictions on scrap tire disposal will also need to be taken into account in the investment decision making process.

Finally, it should be noted that a saving on capital of about 14 percent can be effected if marketing arrangements can be made such that storage facilities for the oil and gas are not required. This situation, along with other economies associated with larger scale (e.g., a 150 t/d plant) operation, would improve the economic picture of this process.

TABLE 4.10. CASE ANALYSIS SHEET FOR A MOLTEN SALT PYROLYSIS PLANT SIZED FOR A TIRE THROUGHPUT RATE OF 22,500 T/YR

Tires	20 $/tr	
Purification	30%	
Fuels	4%/MM Btu	
Carbon Black	18¢/lb	
REVENUES		MM $/YR
C_2H_4, C_3H_6, C_4H_8, BTX		1.134
Fuels		1.29
Carbon Black		3.58
TOTAL REVENUES		6.004
Less 10% SAR		.600
NET REVENUE		5.404
OPERATING COSTS		
Base (from Table 4.3)	3.941 MM$/YR	
Purification	.34	
Tire raw materials	.45	
TOTAL OPERATING COSTS		4.731
Gross profit		0.673
Less 46% income tax		0.310
After-tax profit		0.363
% return on $6.93 MM investment		5.24

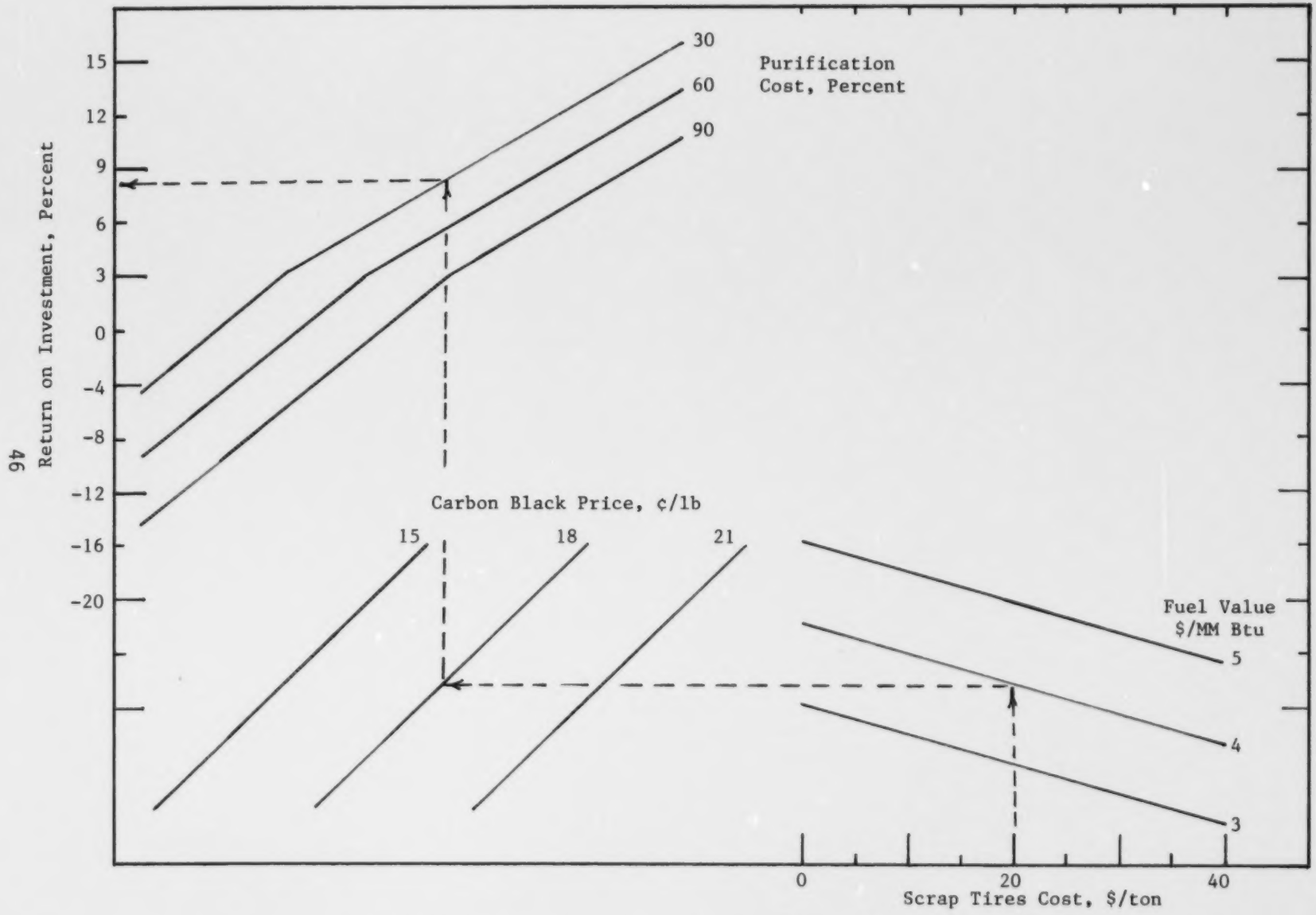


Figure 4.1 Estimated Profitability of a Molten Salt Pyrolysis Plant with a Scrap Tire throughput Rate of 22,500 tons/yr, based on late 1979 Prices and Costs.

5.0 BENCH-SCALE EXPERIMENTAL RESULTS AND DATA BASE

A sufficient quantity of data concerning molten salt pyrolysis of rubber tires is not available in the literature to provide a sound basis on which to design and evaluate a conceptual, commercial, molten salt pyrolysis tire processing plant. An experimental, bench-scale program was therefore developed in order to provide the data required for the layout of and economic evaluation of a conceptual plant. Specific primary objectives of the experimental program were as follows:

- Establish gas, oil, and carbon black yields as a function of pyrolysis temperature, in the range of 330-400°C.
- Establish contact times required to effect completion of the reaction.
- Determine the character of the carbonaceous residue with respect to separability of fiberglass cord and, its friability and washability with respect to chloride removal.
- Determine the character of the oil product with respect to aromatic content, chloride content, heating value, and distillation curve.
- Establish the olefinic content of the gaseous product.
- Determine the extent to which the zinc chloride salt maintains its effectiveness in promoting the reaction. In other words, establish the extent to which the salt can be reused in the reactor, without cleanup.

The extent to which these objectives were met is shown in this Section, along with the data used in the development of the conceptual plant design described in Section 3.0.

The experimental approach used to obtain the data has been described in earlier project progress reports, but will be repeated here in outline form for convenience. A molten salt flow experiment was designed to approximate contact conditions that might be achieved in a commercial reactor, as shown in the experimental layout (Figure 5.1). The reactor consisted of a 2-inch i.d., 316 SS tube with a working section 12 inches long. Stainless screens across each end of the reactor held the rubber charge in place. Salt was preheated in an elevated reservoir to, or slightly above, the reaction temperature, and allowed to drain by gravity through a 5/8-inch i.d. stainless line, through the reactor, to a stainless, heated receiver. It was

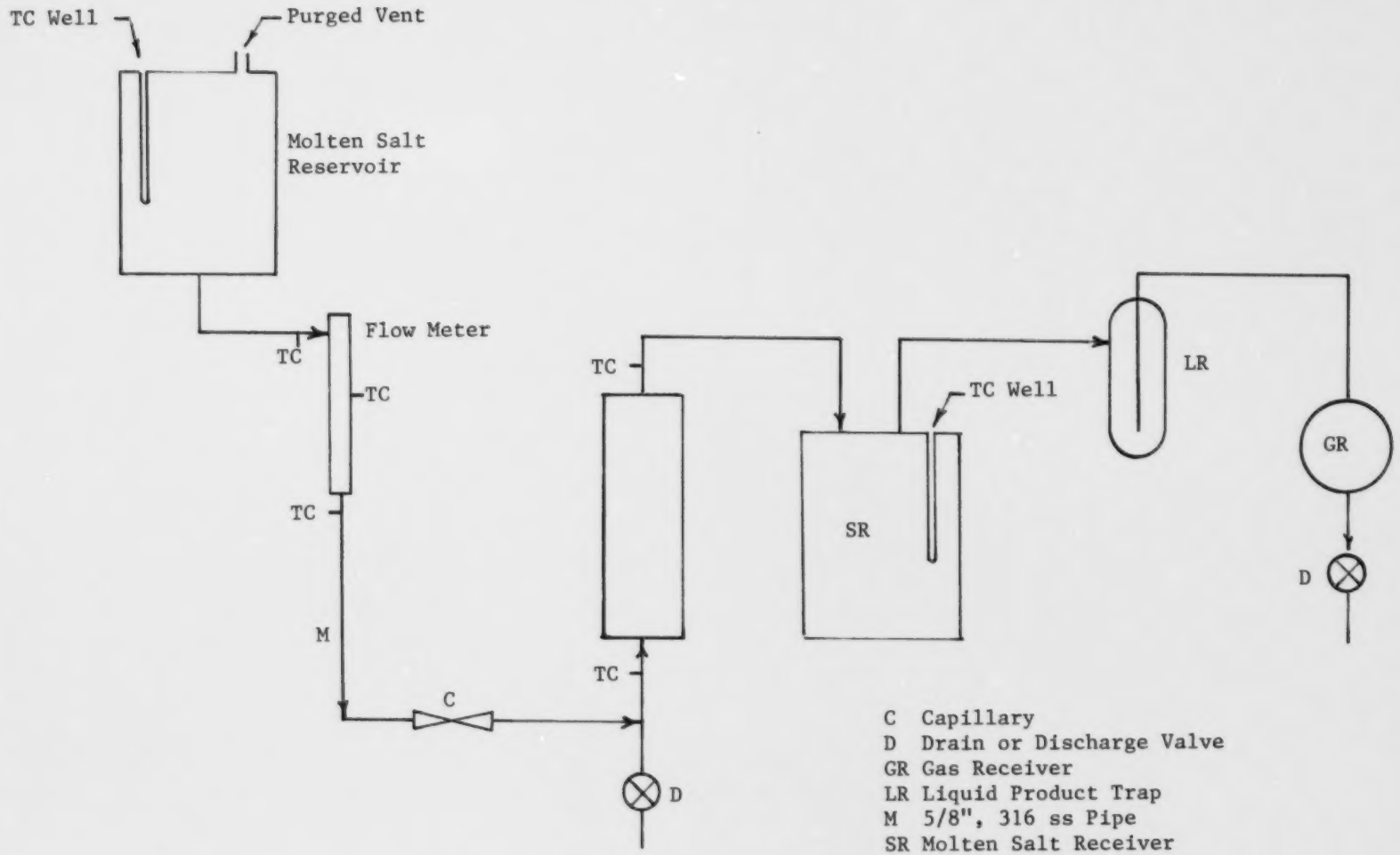


Figure 5.1 Bench Scale Flow Experiment Layout.

necessary, of course, to preheat the flow lines and the reactor in order to keep the salt in a molten state as it moved through the system. This was done by wrapping the system with electric heating tape and insulating all lines and the reactor with a calcium silicate insulation material. The vapor reaction product was swept from the reactor with the salt, with the oil being condensed in a cold trap downstream of the salt receiver. The gaseous product was collected by water displacement from a 35-liter container. Thermocouples were provided at the reactor inlet and outlet as well as in the salt reservoir and receiver.

The salt reservoir and receiver vessels had a capacity of about 30 lb of salt. However, most of our runs, especially the later ones, employed a salt charge of about 12 to 15 lb of salt.

In our first experiments, we cut cubes of rubber (about 3/8-inch on a side) from the tread of a tire carcass for the reactor charge. We had considerable difficulty operating the reactor system with this type of charge, primarily because the carbon reaction residue was so friable that small particles of carbon and pieces of fiberglass would break free of the larger chunks and be swept against the reactor outlet screen where they would lodge, eventually accumulating to the point of blocking the flow and stopping the experiment. It sometimes appeared that the reaction was occurring so fast that gas pressure within a piece of rubber was building up to the point of explosively shattering the structure, thus producing the smaller particles and freeing the glass fibers which would eventually plug the reactor.

The experimental system operated much more successfully and reproducibly, however, when the reactor was charged with strips of rubber cut from a tire, each about 3/8 x 1/2 x 12 inches in size. These strips were packed longitudinally in the reactor, with a total charge weight in the range of 150 to 170 grams. Less reactor plugging was encountered with rubber pieces in this size range and shape, which is attributed to there being less rubber surface area, hence slower overall reaction rate, and to the fact that the fiberglass was in longer strands than in the earlier experiments so that there was less of a tendency for it to be swept to the reactor outlet screen structure.

A total of 24 experimental runs were made in the bench-scale flow apparatus, runs No. 18-24 being made with strips of rubber rather than cubes. These latter runs gave the better, more consistent, results, and therefore are considered more reliable for use as a basis for the formulation and evaluation of a conceptual commercial process. The yields and other data from this latter series of runs (Nos. 18-24) will therefore be summarized in this Section as it relates to the plant design process, Section 3.0. Results from the earlier runs, 1-17, were reported in progress reports.

A decision was taken early in the project to limit the experimental work to use of zinc chloride as catalytic and heat transfer agent, although prior work had indicated other molten salts are also effective in promoting the rubber pyrolysis reaction (Larsen and Chang, 1976). Factors that were important in the taking of this decision were the relatively low cost of zinc chloride compared with some other salts, its moderate melting point (~290°C),

the relatively large number of corrosion investigations made with this salt in connection with the Consol Synthetic Fuels (CSF) project (DCR Report No. 39, 1969), and the limited amount of resources available to the current project. It was therefore necessary to keep the scope of the present investigation relatively narrow. The experimental work reported on here was therefore limited to rubber pyrolysis in molten zinc chloride.

5.1 PRODUCT YIELDS AND CHARACTERIZATION

The most successful runs (e.g., no plugging problems, reasonably steady temperature maintenance, and acceptable material balance closures) of the flow apparatus insofar as providing product yield data were runs 18-21. Data sheets for these runs are summarized in this Section. Data sheets for experimental runs previous to those summarized here are contained in the project quarterly reports.

Table 5.1 shows the yield of gas, oil, and residue (carbon black plus fiberglass) from runs 18-21. The average percentage yields are shown in Table 5.2, where it can be seen that the gas, oil, and crude residue yields are 17.9, 30.7, and 52.1 percent, respectively. The total yield of 100.7 percent is attributed to chloride contamination of the oil and residue.

The material balances by run are shown in Table 5.3. The largest deviation is +7.0 percent (run 21), where the average for the four runs is +0.7 percent. The slightly larger yield weight than charge weight of +0.7 percent is thought to be due to chloride contamination of the oil and residue. These material balance closures are considered quite good in view of the relatively small scale of the experiments and in view of the nature of the reaction, which produces products of three phases (gas, liquid, and solid), one of which (solid) is difficult to recover, as some carbon particles are carried to the salt reservoir with the molten salt.

The gaseous yields by component are shown in Table 5.4. Methane is the component in greatest abundance (50.1 percent) although substantial yields of ethane, ethylene, propane, and propylene are also obtained. The gaseous products of greatest commercial value are the olefins: ethylene (17 percent), propylene (5.9 percent), and 1-butene (1.1 percent).

The oil analyses by major component class (aromatics, olefins, and paraffins) are shown in Table 5.5, as determined by NMR spectroscopy. Elemental analyses of the oil from various runs are shown in Table 5.6. Heating values of the crude oil are shown for a number of runs also. The chloride content of the oil varied from a low of about 0.04 percent (run 8) to a high of 2.06 percent (run 19). A more typical value is about 0.39 percent (run 18). Distillation curves for the oil were estimated in terms of chromatographic results, as shown in Figure 5.2, for four oil samples. Three of these samples were for runs (7, 8, and 10) which were at conditions similar to the runs whose yields we are using as a basis for the conceptual design plant. We therefore take this oil as being representative of the oil from runs 18-21. The oil is essentially 100 percent distilled at a temperature of 480°C (895°F).

TABLE 5.1. PRODUCT YIELDS FROM MOLTEN ZINC CHLORIDE PYROLYSIS OF SCRAP RUBBER

Run No.	Ave. Reactor Temp, °C	Charge Wt, g	Product Oil Vol, ml	Product Oil Wt, g	Product Gas Vol, l	Product Gas Wt, g	Residue Wt, g
18	360.	183.5	70.	62.1	29.5	30.6	87.2
19	365.	158.7	51.	43.2	22.	23.6	88.1
20	353.	154.5	50.	45.	31.	32.5	77.5
21	390.	160.5	57.	51.5	32.	30.7	89.5

Average Oil Density = 0.885 g/ml

TABLE 5.2. AVERAGE PERCENTAGE YIELDS OF THE PRINCIPLE PRODUCT CLASSES, MOLTEN ZINC CHLORIDE PYROLYSIS OF SCRAP RUBBER. RESULTS ARE FROM RUNS 18-21

Product Class	Total Yield, grams	Yield*, %
Gas	117.4	17.9
Oil	201.8	30.7
Residue	342.3	52.1
TOTAL	661.5	100.7

*Based on total rubber charged of 657.2g

TABLE 5.3. MATERIAL BALANCES ON RUNS 18-21, MOLTEN ZINC CHLORIDE PYROLYSIS OF SCRAP RUBBER

Run No.	Rubber Charged, g	Yields, g				Residue, Wt %
		Oil	Gas	Residue	Total	
18	183.5	62.1	30.6	87.2	179.9	98.
19	158.7	43.2	23.6	88.1	154.9	97.6
20	154.5	45.	32.5	77.5	155.	100.3
21	160.5	51.5	30.7	89.5	171.7	107.0

Average Wt % Recovered = 100.7

TABLE 5.4. CHROMATOGRAPHIC ANALYSIS OF THE GASEOUS PRODUCT, FROM MOLTEN ZINC CHLORIDE PYROLYSIS OF SCRAP RUBBER

Run No.	Component Mole Fraction						
	Methane	Ethane	Ethylene	Propane	Propylene	Isobutane	1-Butene
18	.491	.163	.211	.057	.0469	.015	.0156
19	.444	.173	.209	.0713	.0562	.0347	.0114
20	.498	.177	.150	.060	.068	.032	.015
21	.571	.195	.110	.054	.065	.004	.001
Ave.	.501	.177	.170	.061	.059	.021	.011

TABLE 5.5. ANALYSIS OF THE PRODUCT OIL FROM MOLTEN SALT PYROLYSIS OF SCRAP RUBBER

Run No.	Component, Vol. %			H/C Ratio (From NMR)
	Aromatics	Paraffins	Olefins	
18	24.84	60.35	14.81	1.58
19	29.25	57.35	13.39	1.5
Ave.	27.05	58.85	14.1	

TABLE 5.6. ELEMENTAL ANALYSES AND HEATING VALUES OF THE PRODUCT OIL

Run No.	Elemental Analysis, Wt %					Heating Value, Btu/lb
	C	H	S	N	Cl	
3	87.83	10.80	0.31	0.061	0.12	17,590
4	85.40	9.78	0.42	0.069	0.52	18,320
5	88.34	10.46	0.54	0.026	0.16	18,510
6	83.62	9.42	0.39	0.029	0.14	18,690
7	88.36	10.91	0.45	0.031	0.12	18,560
8	86.99	10.90	0.34	<0.01	0.04	18,710
9	85.53	10.24	0.11	0.04	0.14	18,420
10	88.28	10.39	0.46	0.026	0.06	18,600
11	87.83	10.58	0.57	0.14	0.08	18,510
12	88.02	10.49	0.41	0.05	1.01	
13	89.01	10.42	0.30	0.04	0.26	
14	85.79	10.48	10.51	0.50	1.22	
15	88.30	10.44	0.37	0.02	0.61	18,200
16	87.84	10.16	0.65	0.82	0.12	18,580
17B	83.75	9.49	0.31	0.008	0.52	17,900
18	88.20	10.65	0.51	0.03	0.39	18,500
19	86.51	10.25	0.51	0.95	2.06	

Figure 5.2 Photograph of Typical Strips Cut From the Tread of a Rubber Tire. Strips such as these were inserted longitudinally into the reactor.

Elemental analyses of the carbon black from two runs are shown in Table 5.7. Most of the rubber sulfur apparently stays in the carbon black, although it also occurs in the oil in amounts from 0.3 to 0.5 percent (see Table 5.6). The chloride content of the carbon black depends on numerous factors among which an important one is the manner and extent to which it is washed. The high value of 1.6 percent, Table 5.7, may have been due to inadequate washing. Lack of time during this experimental program prevented us from exploring this important question thoroughly.

Carbon black from runs 18-23 was blended into two samples (runs 18 and 19 into Sample T-1 and runs 21 and 23 into Sample T-2). These samples were characterized with respect to their carbon black properties, courtesy of the Cabot Corporation (McCaffrey, 1979, 1980). The results of their tests are contained in Table 5.8. These results indicate the carbon black recovered from rubber tires by the molten salt pyrolysis process is unlike most known commercial carbon blacks. However, no attempt was made to reduce the particle size of the test samples to the size range of commercial carbon blacks. The marketability of this carbon black has not been demonstrated, so a prime objective of any future work on this process should be to generate sufficient carbon black for this purpose.

5.2 PROCESS CONDITIONS

Establishing precise values for process conditions such as reaction temperature and contact times in a system such as molten salt pyrolysis of rubber is difficult because of the need to preheat the flow lines and reactor in order to prevent solidification of the salt. This preheat period also causes some pyrolysis of the rubber in the reactor. The heatup period required to bring the experimental system up to reaction temperature was of the order of three to four hours. Our procedure was to bring the flow lines

TABLE 5.7. ELEMENTAL ANALYSES OF THE PRODUCT CARBON BLACK

Run No.	Elemental Analysis, Wt %				
	C	H	O	S	Cl
18	87.14	2.28	4.84	2.10	0.94
19	76.31	2.65	9.14	2.03	1.60

TABLE 5.8. ANALYTICAL TEST RESULTS ON CARBON BLACK FROM SCRAP TIRES (McCaffrey, 1979, 1980)

Measurement	Sample No. T1 Value	Notes	Sample No. T2 Value	Notes
ASTM Iodine No., mg/g	155	(1)	152	
Dibutyl Phthalate Absorption, cc/100g	61.2	(2)	-	(4)
Nitrogen Surface Area, m^2/g	25.		41.	
Tinting Strength, %ITRB	34.9	(3)		
Ash, %	12.2		10.6	
Volatiles, %	13.8		14.4	
Density, lb/ft^3	31.2		35.3	
Elemental Analysis				(5)
Total Sulfur, %			1.56	
Carbon, %			72.6	
Hydrogen, %			0.91	
Oxygen, %			-	
Nitrogen, %			0.08	

(1) Iodine Number Test inaccurate due to high ash. N_2SA value is representative of true surface area.

(2) Modified DBPA Test - not according to ASTM, due to machine not responding to torque increase as with normal carbon black. Estimated value only.

(3) Tint paste was "gritty".

(4) Unable to obtain DBPA value on either 20g or 25g sample. Machine would not sheet off - not sufficient torque.

(5) Values may be low. Sample losing volatiles at the rate of 30 µg/min. Results corrected for volatile loss but error possible.

NOTE: The recovered black was not de-ashed prior to the analysis. The high ash content would tend to increase the density, depress tint and N_2SA.

and reactor up to temperatures in the range of 527-572°F (275-300°C), and initiate the salt flow by thawing a salt plug in the exit line from the salt reservoir. During this heat-up period, small amounts of gas would be evolved and collected in the gas reservoir. When the salt, typically in the temperature range of 716-770°F (380-410°C), entered the reactor, the reactor thermocouples would respond, and the gas evolution rate would increase markedly, as shown qualitatively by the curve in Figure 5.3. The thermocouple response tended to lag behind the gas evolution rate. As the reaction proceeded toward completion, the gas rate tailed off sharply. The salt-rubber contact time required for completion of the reaction was therefore estimated as that period between the initial, marked increase in gas evolution rate and the tailing off of the gas production rate, as depicted in Figure 5.3. These times and corresponding average reactor temperatures are shown in Table 5.9, for runs 18-21. The data are too imprecise to determine a reasonably exact relationship between reaction time and temperature, but qualitatively, the required contact time appears to decrease as the temperature is increased, as expected. Also, the reactions are essentially over in less than two minutes in this temperature range (353-390°C), with the rubber preheated as described above.

In a commercial-scale operation of the type described in Section 3.0, where the rubber is heated by contact with hot salt, a longer contact time between molten salt and rubber would be required than in experiments of the bench-scale type. It is estimated here that contact times of the order of ten minutes should be adequate for heat-up and reaction, but this value should be confirmed in a pilot-type operation before the firming up a commercial plant design.

5.2.1 Effect of Reaction Temperature on the Oil and Gas Yield

The total weight of the oil and gas produced, as a fraction of the weight of the rubber charged, is shown in Table 5.10 and Figure 5.4, for runs 18-21. The results indicate a slight increase in oil and gas yield with increasing reaction temperature in this range (353-390°C). One would, therefore, expect the carbon black residue which is produced at the higher reaction temperatures to contain less volatile matter, although the results shown in Table 5.8 do not indicate this to be the case. The data scatter apparently is sufficient to mask any trend which may exist in this temperature range, so one is unable to draw a conclusion with this limited amount of data.

5.2.2 Methane and Ethylene Yields

There is considerable scatter in the data, but the results shown in Tables 5.11 and 5.12 and in Figures 5.5 and 5.6 indicate the methane yield is increased with increased reaction temperature whereas the ethylene yield is decreased with increasing temperature. These results confirm what one would expect from the pyrolysis of hydrocarbon gases in this temperature range. There may be an optimum reaction temperature for maximizing the yield of the olefin gases and for optimizing the carbon black quality (e.g., the volatile

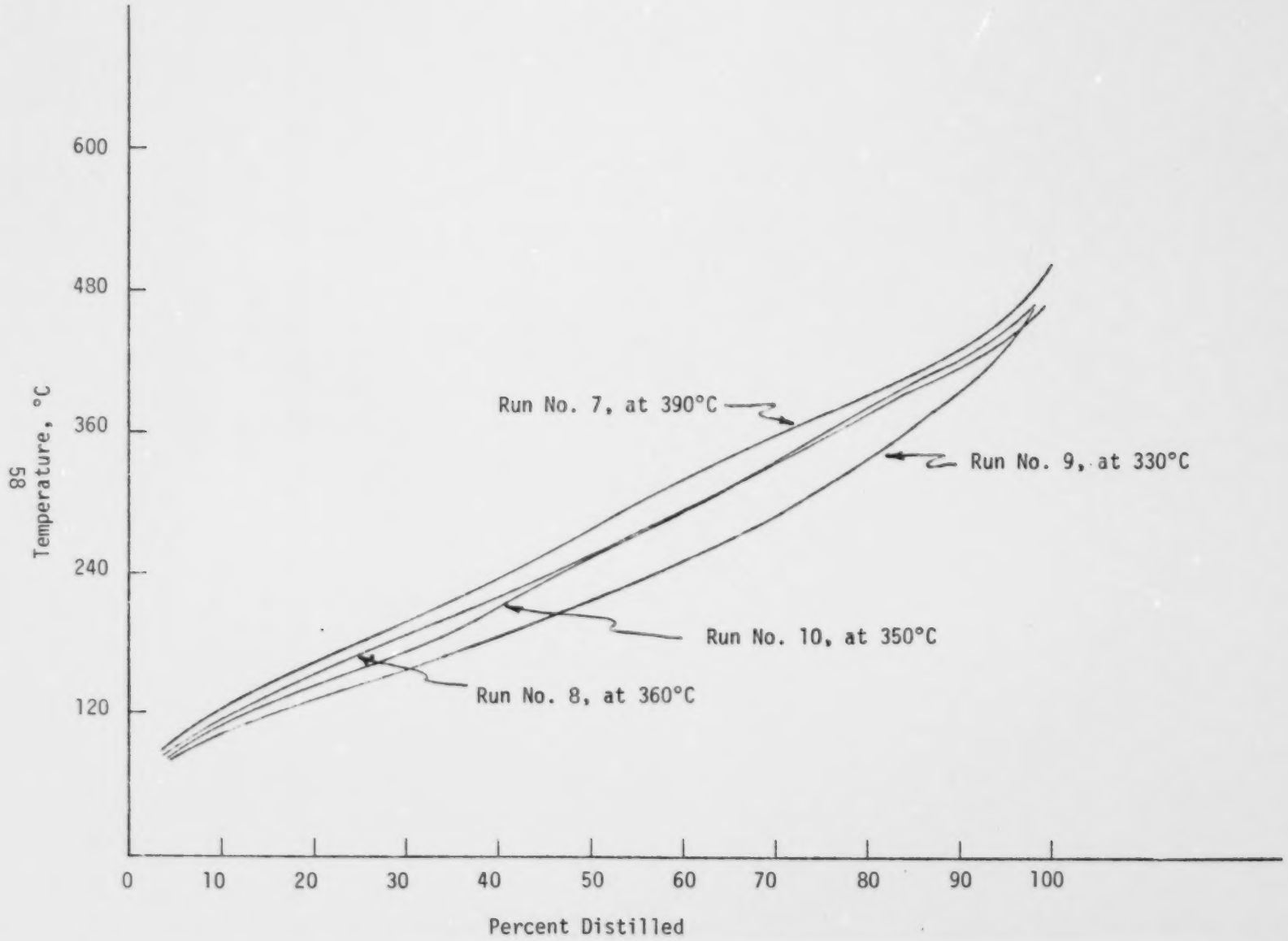


Figure 5.3 Distillation Curves for the Oil Produced by Molten Salt Pyrolysis of Scrap Rubber Tires.

TABLE 5.9. PROCESS CONDITIONS FOR MOLTEN SALT PYROLYSIS OF RUBBER

Run No.	Temperature, °C			Contact Time*, seconds
	Min	Max	Average	
18	360	360	360	110
19	360	370	365	100
20	345	360	353	120
21	390	390	390	100

*Defined as time between beginning of rapid gas evolution, and decrease of gas production.

TABLE 5.10. FRACTIONAL YIELD OF THE PRODUCT OIL AND GAS, FOR BENCH-SCALE EXPERIMENTAL RUNS 18-21

Run No.	Average Reaction Temperature, °C	Fractional Oil and Gas Yield
18	360	0.505
19	365	0.421
20	353	0.502
21	390	0.512

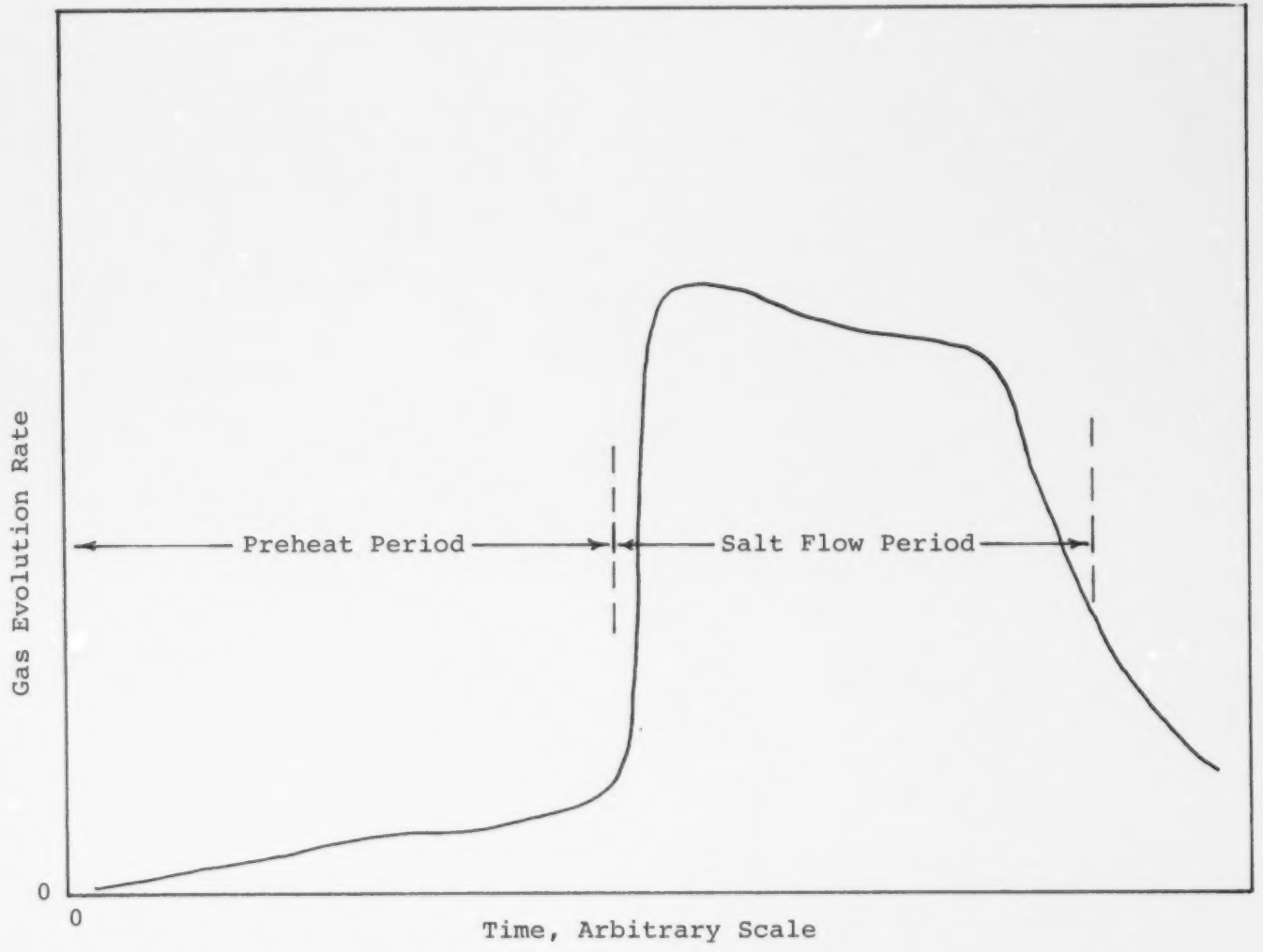


Figure 5.4 Qualitative Gas Evolution Rate Curve, Molten Salt Pyrolysis of Rubber in the Flow Reactor.

TABLE 5.11. METHANE YIELD AS AFFECTED BY REACTION TEMPERATURE, FOR RUNS 18-21

Run No.	Average Reaction Temperature °C	Methane Yield	
		Volume Percent of the Gas	Wt. Percent of Rubber Charged
18	360	49.1	5.2
19	365	44.4	4.0
20	353	49.8	6.5
21	390	57.1	7.4

TABLE 5.12. ETHYLENE YIELD AS AFFECTED BY REACTION TEMPERATURE, FOR RUNS 18-21

Run No.	Average Reaction Temperature °C	Ethylene Yield	
		Volume Percent of the Gas	Wt. Percent of Rubber Charged
18	360	21.1	3.9
19	365	20.9	3.3
20	353	15.0	3.5
21	390	11.0	2.5

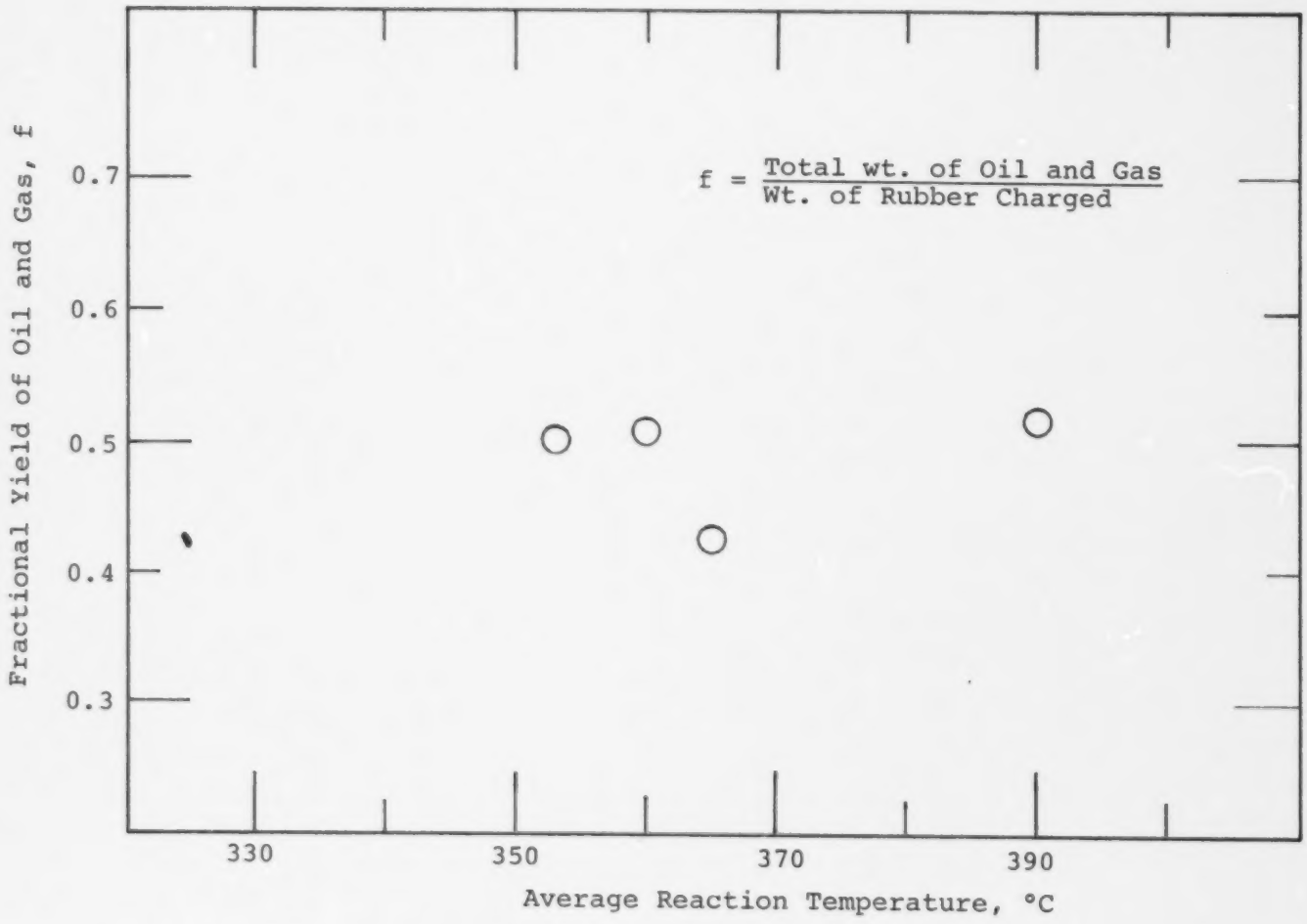


Figure 5.5 Effect of Temperature on the Yield of Oil and Gas.

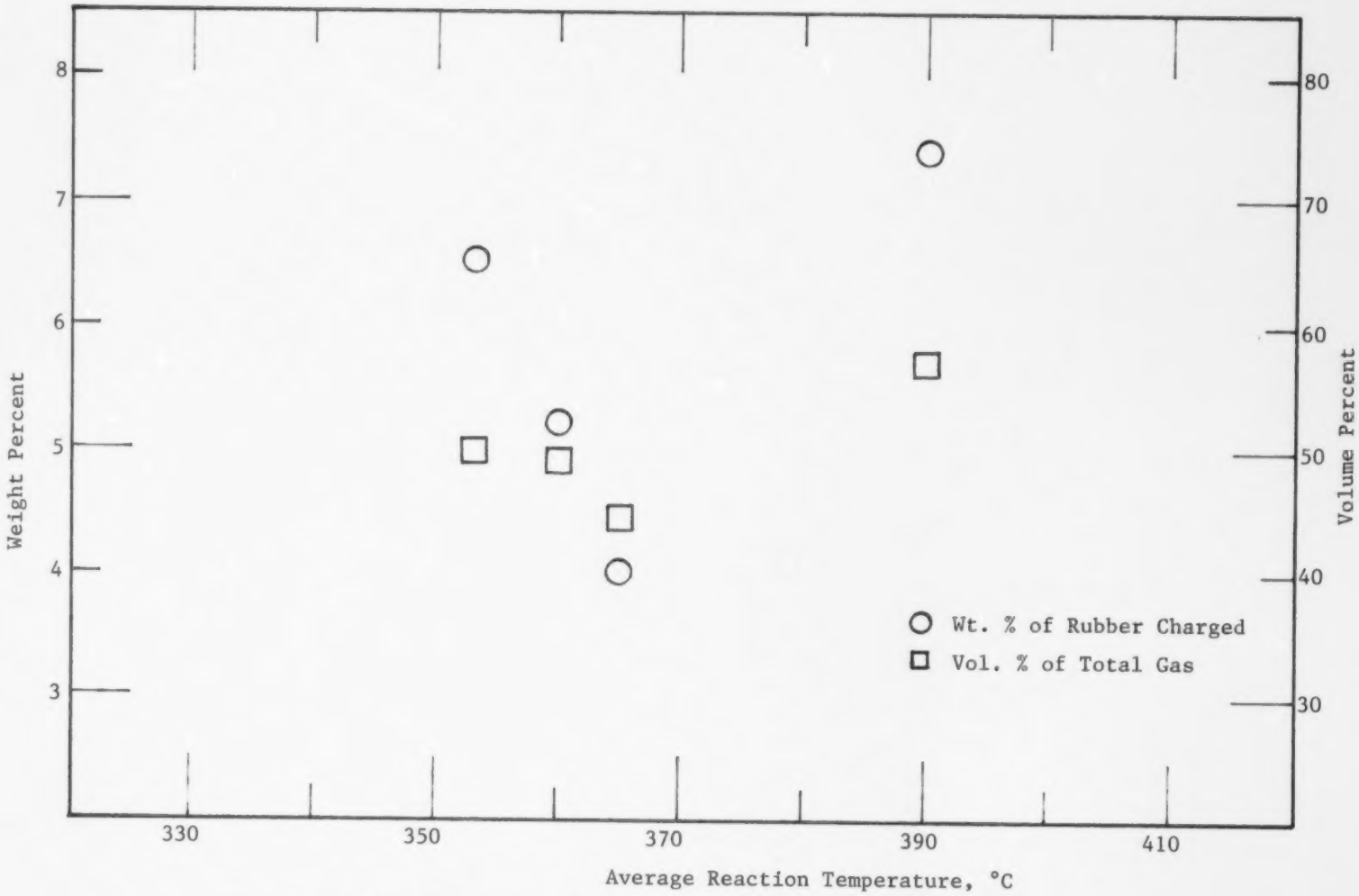


Figure 5.6 Effect of Reaction Temperature on the Methane Yield.

content), but insufficient data were obtained in this investigation for exploring this question thoroughly.

5.3 RUNS WITH USED SALT

The economics of a pyrolysis process of this type would be improved considerably if the salt could be reused repeatedly without cleanup, or "regeneration". We, therefore, initated a series of runs, Nos. 22-24, in order to determine whether or not the salt could be reused without cleanup. After use, the salt contains some carbon black particles and probably other impurities picked up in the system.

Run 22 was not completed because of burnout of the heating tape. THe results for runs 23 and 24 are summarized in Tables 5.13 and 5.14. The average percentage yields for the reused salt runs are compared with the yields from the fresh salt runs in Table 5.15. The gas, oil, and residue yields compare within the experimental data scatter, although the gas and oil yields appear slightly low for the reused salt runs. However, we feel the low values are due to a small vapor leak which was detected during run No. 24. It therefore appears that the salt can be reused at least three times without appreciable effect on the yield of the principal product classes. It would be desirable to investigate the effectiveness of used salt in additional runs in any future work.

5.4 CHANGE IN OIL COMPOSITION WITH AGE

The product oil from this process appears to be somewhat unstable, as we accidentally discovered through re-analysis of two of the oil samples after they had aged at room temperature for several months. The results are shown in Table 5.16 and the NMR spectrograms for Sample No. 18 are shown in the Appendix. The aromatic content of these samples appears to increase with age, while the paraffin content decreases. The changes are not large, but are probably greater than the measurement error. This change is of interest because the aromatics are the components of greatest commercial value, although it is unlikely that advantage can be taken of this result unless a way can be found to accelerate this aging process.

TABLE 5.13. YIELD DATA FOR BENCH-SCALE EXPERIMENTAL RUNS IN WHICH THE ZINC CHLORIDE SALT WAS REUSED

Run No. Run No.	Average Reaction Temperature, °C	Wt Rubber Charged, g	Yields					Total Wt Recovered, g	Wt % Recovered
			Oil		Gas		Residue, g		
			Vol, ml	Wt g	Vol, l	Wt, g			
23*	360	167.5	61.5	55.5	30	30.5	90	176	105.1
24+	365	157.5	50. **	42.7	21**	21.4	82	146.1	92.8

* Second use of salt, without cleanup

\+ Third use of salt, without cleanup

** Low, due to a slight leak

TABLE 5.14. PERCENTAGE YIELDS OF THE PRODUCTS, WITH REUSED MOLTEN ZINC CHLORIDE

Run No.	Yields, Wt % of Rubber Charged		
	Oil	Gas	Residue
23*	33.1	18.2	53.7
24+	27.1	13.6	52.1
Average	30.2	16.0	52.9

*Second use of the salt, without cleanup

+Third use of the salt, without cleanup

TABLE 5.15. COMPARISON OF PRODUCT YIELDS, EXPERIMENTAL RUNS WITH FRESH SALT AND RUNS WITH REUSED SALT

Product Class	Yields, wt %	
	Avg of Runs with Fresh Salt	Avg of Runs with Re-used Salt
Gas	17.9	16.0
Oil	30.7	30.2
Residue	52.1	52.9
Total	100.7	99.1

TABLE 5.16. CHANGE IN OIL COMPOSITION WITH AGE, ACCORDING TO NMR ANALYSIS

Sample No.	Composition, Volume %					
	Aromatics		Paraffins		Olefins	
	Sept. 79	June 80	Sept. 79	June 30	Sept. 79	June 80
18	24.84	26.03	60.35	56.0	14.81	17.97
19	29.25	35.02*	57.35	51.86*	13.39	13.12*

* With TMS as solvent

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7.0 APPENDICES

7.1 OIL ANALYSES (Galbraith Laboratories)

7.2 CARBON BLACK ANALYSES (Galbraith Laboratories)

7.3 DATA SHEETS FOR BENCH-SCALE RUNS NOS. 18-24

7.4 SOLUBILITY OF ZINC CHLORIDE IN WATER

7.5 ZINC CHLORIDE CORROSION OF 316 SS, FROM OCR REPORT 39, VOL. III, BOOK 1

7.6 NMR SPECTRA FOR THE OIL FROM RUN NO. 18